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Development of a high-throughput method for the optical screening of phase transformations related to amorphous materials for harsh environment applications

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14. ABSTRACT

A method to systematically and efficiently search for new materials is to use thin-film combinatorics, which offers the great advantage of producing materials libraries with hundreds of samples on one substrate in a single experiment. Using a combinatorial approach together with high-throughput characterization methods should lead to faster results than using the conventional experimental strategies. This project's objective is to fabricate thin film materials libraries of amorphous materials which exhibit high crystallization temperatures and show superior corrosion resistance, and to develop high-throughput methods to characterize them. Combinatorial libraries of two materials systems were studied during the course of this project: Ti-Ni-Cu and Cr-Si-Nb. Physical vapor deposition was used to deposit the libraries. Atomic mixing and partial layer/atomic layer approaches for coating material growth were both used. A series of identical thin-film libraries were produced, enabling directly comparable subsequent measurements during annealing and high-temperature oxidation corrosion investigations. High-throughput characterization techniques developed and/or employed included automated surface profilometry, automated energy dispersive x-ray spectroscopy, automated x-ray diffraction, high-throughput transmission electron microscopy, automated electrical resistivity mapping, in-situ measurement of bending of micro-machined cantilever beams, ex-situ digital holographic measurement of thickness changes or cantilever bending, and in-situ optically monitored surface roughness, color, or reflectivity changes during heat treatment. These techniques offer potential to rapidly characterize materials libraries to identify promising candidates with desired properties.

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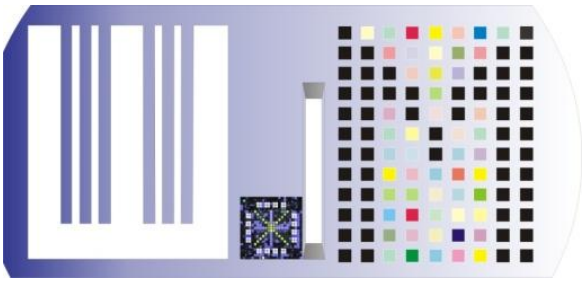

Final report

Development of a high-throughput method for the optical screening of phase transformations related to amorphous materials for harsh environment applications

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Executive Summary

There is an increasing demand for new or optimized materials to enable the continuous further development of technologies. The requirements of these materials are getting more and more challenging since the fields of application are broadening. Especially from industry, there is a high interest in materials that can operate in harsh environments such as with high temperatures and corrosive atmospheres.

An example of this is “bulk metallic glass” which is a class of materials with outstanding properties such as remarkable formability, elasticity, strength, and corrosion resistance. For instance, researchers have made metallic glass that is three times stronger than the best industrial steel and ten times springier.

A method to systematically and efficiently search for new materials is to use the thin-film combinatorial technique, which offers the great advantage of producing materials libraries with hundreds of samples on one substrate in one experiment. Using a combinatorial approach together with high-throughput characterization methods should lead to faster results than using the conventional one-at-a-time strategy. This projects’ objective is to fabricate thin film materials libraries of amorphous materials which exhibit high crystallization temperatures and show superior corrosion resistance, and to develop high-throughput methods to characterize them.

Combinatorial libraries of two materials systems were studied during the course of this project:

Ti-Ni-Cu: a shape memory alloy in some compositions, it can also have an amorphous composition region.

Cr-Si-Nb: the ternary phase diagram indicates a composition region with strong suppression of melting/stabilization of the liquid.

Physical vapor deposition was used to deposit the libraries. Atomic mixing and partial layer/atomic layer approaches for coating material growth were both used. Highly reproducible batches of 5 identical thin-film libraries were produced, enabling directly comparable subsequent measurements, annealing and high-temperature oxidation corrosion investigations.

High-throughput measurement and characterization techniques used and/or developed are:

- Surface profilometry (stylus method) of lift-off structured substrates (automated mapping).
- Energy dispersive x-ray microprobe (EDX) for elemental composition (automated mapping).
- X-ray diffraction (XRD) for crystallographic/amorphous analysis (automated mapping).
- High-throughput transmission electron microscope (TEM) sample preparation using MEMS structures (micro/nano-structure identification).
- Electrical resistivity vs. temperature, which can be correlated to thin film phase and microstructure (automated mapping, development of *in-situ* measurement and mapping).
- *In-situ* measurement of bending in micromachined cantilever arrays (thin film stress change during annealing – which may be correlated to phase transitions – or corrosion)
- *Ex-situ* digital holographic measurement of thickness change or cantilever bending (corrosion and thin film stress change, respectively).
- *In-situ* optically-monitored surface roughness, color or reflectivity changes during heat treatment (amorphous to crystalline state change, corrosion).

Combinations of these high-throughput techniques must be available, depending on the materials and properties being investigated, and the testing conditions and environments that are applied.

1.0. Introduction

There is an increasing demand for new or optimized materials to enable the continuous further development of technologies. The requirements of these materials are getting more and more challenging since the fields of application are broadening. Especially from industry, there is a high interest in materials that can operate in harsh environments such as with high temperatures and corrosive atmospheres.

Recently the class of “bulk metallic glasses” is becoming more and more popular due to outstanding properties such as remarkable formability, elasticity, strength and corrosion resistance. For example, researchers have made metallic glass that is three times stronger than the best industrial steel and ten times springier.

The key to this behavior is due to the fact that these materials are non-crystalline compared to the “standard” metals which have a crystalline structure with a short range and long range order. Due to the lack of grain boundaries, which can be points of weakness in crystalline materials, the resistance to wear and corrosion is superior. Because of these unique properties, this class of materials seems to be a promising candidate for applications in harsh environments.

To obtain the amorphous phase, the material needs to be rapidly cooled from the liquid phase to suppress the crystallization process, for example using a super-cooled fast spinning wheel. But also vapor deposition (for example sputtering) can lead to amorphous thin metal films. In order to find new interesting amorphous metal materials systems, the thin-film combinatorial approach offers the great advantage of producing materials libraries with hundreds of samples on one substrate in one experiment. Using a combinatorial approach together with high-throughput characterization methods should lead to faster results than using the conventional one-at-a-time strategy.

This projects’ objective is to fabricate thin film materials libraries of amorphous materials which exhibit high crystallization temperatures and show superior corrosion resistance, and to develop high-throughput methods to characterize them. By having a pallet of high throughput measurement and characterization techniques available, ultimately the crystallization temperature T_x of many different systems of thin films and their temperature-corrosion behavior at high temperature in an oxygen-containing environment could be studied. The new methods will be used to provide composition-property maps of the systems under investigation.

2.0. Selection of Materials Systems

The materials systems were selected from an analysis of the literature in the field, from in-house prior knowledge, and by suggestions from researchers from USA. The latter contact was established by Wynn Sanders (EOARD).

Materials systems that were studied in this project are:

Ti-Ni-Cu
Cr-Si-Nb.

Ti-Ni-Cu is a materials system that has been studied in detail in the "*Werkstoffe der Mikrotechnik*" (Materials for Microtechnology) laboratory with regard to its shape memory properties[1, 2, 3]. It is known to have an amorphous region for some compositions when grown by PVD methods on unheated substrates. While it is a quite complex system in terms of phases, crystallization behavior and precipitates, the prior knowledge and experience make it suitable for testing and developing a range of measurement and characterization techniques foreseen in this project, along with the analyses required for interpretation.

The Cr-Si-Nb ternary phase diagram indicates a strong suppression of melting/stabilization of the liquid in the vicinity of 70.0-90.0%, Nb, 5.0-35.0% Cr, and 10.0-25.0 % Si. There was also interest in the effects of small additions of Boron on this alloy system with concentrations in a range of roughly 3-8%, although within the timeframe of this project it could not be explored[4].

3.0. Fabrication of Combinatorial Materials Libraries

Materials libraries are produced by using several combinatorial sputtering systems. In principle the films can be deposited from elemental targets either in co-deposition mode or in a sequential multilayer mode. In the latter mode, the constituent layers of the multilayer having thicknesses in the range between 1 and 10 nm and are repetitively built up to the desired total thickness, typically in the 300 to 1,000 nm range. However for the deposition of amorphous materials, the co-deposition mode should be favored, as due to the direct, atomic-scale mixing of the elements during deposition, the formation of a metastable phase may in some cases be obtained. In the multilayer mode it is more likely that the constituent layers are crystalline, and anyway a post-deposition temperature treatment would be necessary to achieve mixing through the dissolution of the layers. In many instances, this would lead to the nucleation and growth of thermodynamically stable polycrystalline phases, although in some cases an amorphization reaction may occur. An example for the latter is the Ni-Ti system[5].

In view of the developments encountered in the project, it seems to be also of interest to use the multilayer mode; however the individual layers of the multilayer should be as thin as possible in order to achieve a complete mixing of the system without long annealing (diffusion) times that might favor crystallization and growth.

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[1] R. Zarnetta, S. Kneip, Ch. Somsen, A. Ludwig, High-throughput characterization of mechanical properties of Ti-Ni-Cu shape memory thin films at elevated temperatures, Mater. Sci. and Eng. A 528, 6552– 6557.

[2] R. Zarnetta, M. Ehmann, A. Savan, A. Ludwig, Identification of optimized Ti-Ni-Cu shape memory alloy compositions for thin film microactuator applications, Smart Mater. Struct. 19 065032

[3] R. Zarnetta, D. König, C. Zamponi, A. Aghajani, J. Frenzel, G. Eggeler, A. Ludwig, R-phase formation in Ti39Ni45Cu16 shape memory thin films and bulk alloys – discovered by combinatorial methods, Acta Materialia, 57, 4169-4177.

[4] E-mail from G. Wilks CTR USAF AFMC AFRL/RXLMP 29 July 2010.

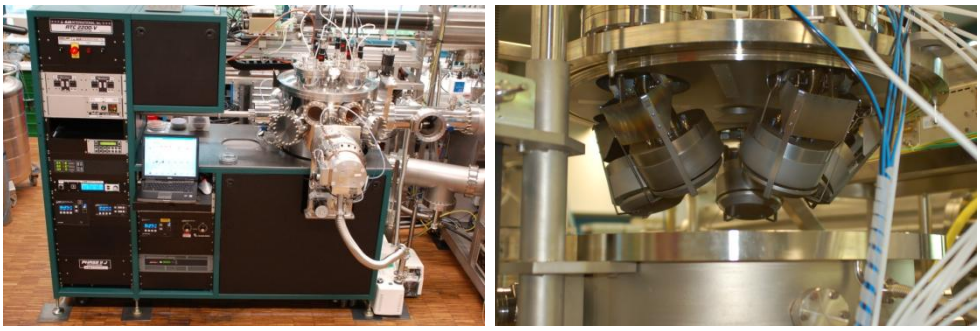
[5] H. Cho, H.Y. Kim, S. Miyazaki, Fabrication and characterization of Ti–Ni shape memory thin film using Ti/Ni multilayer technique, Science and Technology of Advanced Materials 6 (2005), 678–683.

One of the deposition machines is equipped with computer-controlled shutters that can be moved so as to create a well-defined concentration gradient across a 4" high-temperature-stable substrate (fused silica, or Al_2O_3). In another machine, up to 5 sources are simultaneously directed towards the substrate. Due to the system geometry, concentration gradients from each source are naturally produced while the film is growing. In yet a different machine, composition gradients from up to 3 materials can be made with combinations of rotations of the substrate(s) while using apertures to shape the deposition profiles rather than moving blade-shutters. With these techniques, combinatorial libraries were made of the materials being investigated, and then screened to identify those compositions that were amorphous.

For this project it was highly desirable to have the possibility to grow several materials libraries within one experiment. Then each identical materials library could be used for different heat treatments, and the results directly compared. Several additional recent developments with regard to our combinatorial sputtering capabilities have enabled this. We have installed a special multilayer sputter system, where it is possible to coat several 4-inch wafers with identical materials libraries in one experiment. We have also developed a technique to fabricate several small ternary libraries within one 4-inch wafer using an adapted multilayer approach[6].

3.1. Deposition Profiles Resulting from Natural Gradients

The simplest method of making combinatorial materials libraries by physical vapor deposition (PVD) is by using the natural thickness gradients that arise from the geometry of having multiple sources arranged around a static substrate (Figure 1). The angle between the target and substrate surfaces causes a regular change in the deposition rate of material arriving from that source, resulting in a wedge-shaped thickness profile. The sum of the materials gradients over the substrate surface leads to a library of compositions, which can be controlled by adjusting the thickness of the wedge produced by each source.



(a) (b)

Figure 1: (a) Physical vapor deposition machine for the preparation of thin-film combinatorial libraries with the co-sputtering approach. (b) View of 5 confocal magnetron cathodes. The cross-contamination shields that would normally be in place are removed so that the cathodes can be seen.

[6] P. Buenconsejo, A. Siegel, A. Savan, S. Thienhaus, A. Ludwig, Preparation of 24 Ternary Thin Film Materials Libraries on a Single Substrate in One Experiment for Irreversible High-Throughput Studies, ACS Combinatorial Science, 2012, 14, 25-30.

For the investigation of amorphous materials, this co-deposition mode should be favored because the direct, atomic-scale mixing of the elements during film growth is more likely to lead to the formation of metastable phases. However, complete gradients (i.e. 0 at.% to 100 at.% of material from a given source) cannot typically be achieved.

In the case of Nb-Cr-Si, a restricted composition range within the full ternary diagram was suggested: 70.0-90.0 at.%, Nb, 5.0-35.0 at.% Cr, and 10.0-25.0 at.% Si. While the natural gradient approach could not produce a library exclusively in this range, a substantial part of the library could be made up of those compositions.

Figure 2 shows an example of the compositions obtained in one combinatorial library deposited by the co-deposition of elemental Nb, Cr and Si using the natural wedge approach and targeted towards the composition range that was suggested. Because of the fixed geometry of the cathode layout, it is generally not possible to restrict the library to be exclusively within a particular range. However because the library is a continuous film on a 4-inch diameter substrate, a sufficiently large area with the desired compositions can normally be achieved.

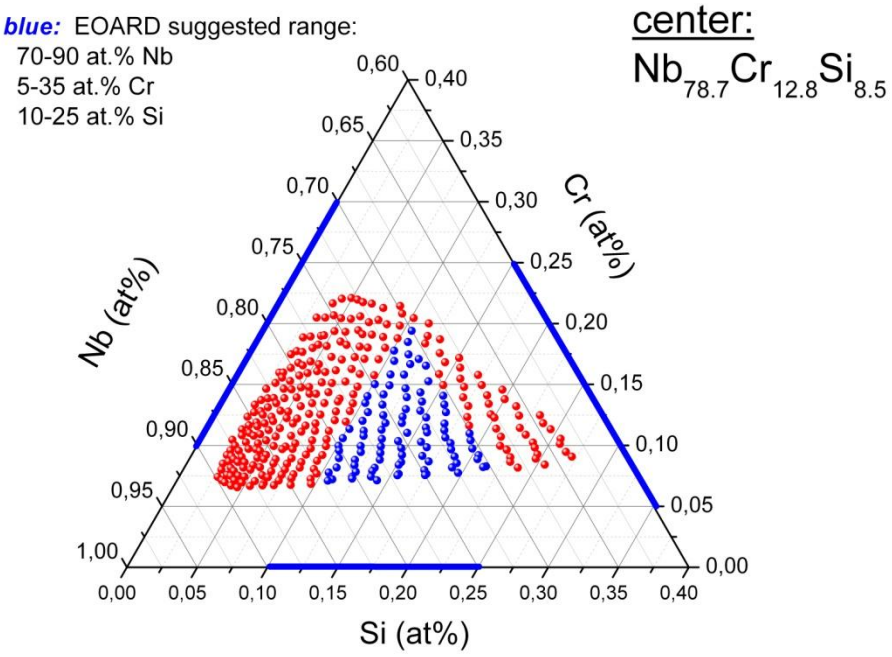


Figure 2: Example of a combinatorial thin-film library produced by co-sputtering from 3 elemental cathodes. Measured composition was determined by automated EDX. The measured points, corresponding to a sampling spot size of approximately Ø0.5 mm, are plotted into a section of the ternary composition diagram. Blue lines along the axes indicate the suggested composition range to explore (Garth Wilks, CTR USAF AFMC AFRL/RXLMP).

3.2. Deposition Profiles Shaped by Moving Shutters

Another method used to fabricate combinatorial thin-film materials libraries is to employ one or more moving blade-type shutters to create a defined thickness gradient by shadowing of the deposition source. By systematically changing the deposition source, a multilayer series of thickness wedges can be formed. Indexed rotations of the substrate align the thickness gradients of the layers of each material to different rotational angles, and a well-defined library can be created. For instance 180° opposing wedges will result in a binary library, and three wedges at 120° to each other make a

ternary library. The PVD chamber being used for this type of deposition is shown schematically in Figure 3.

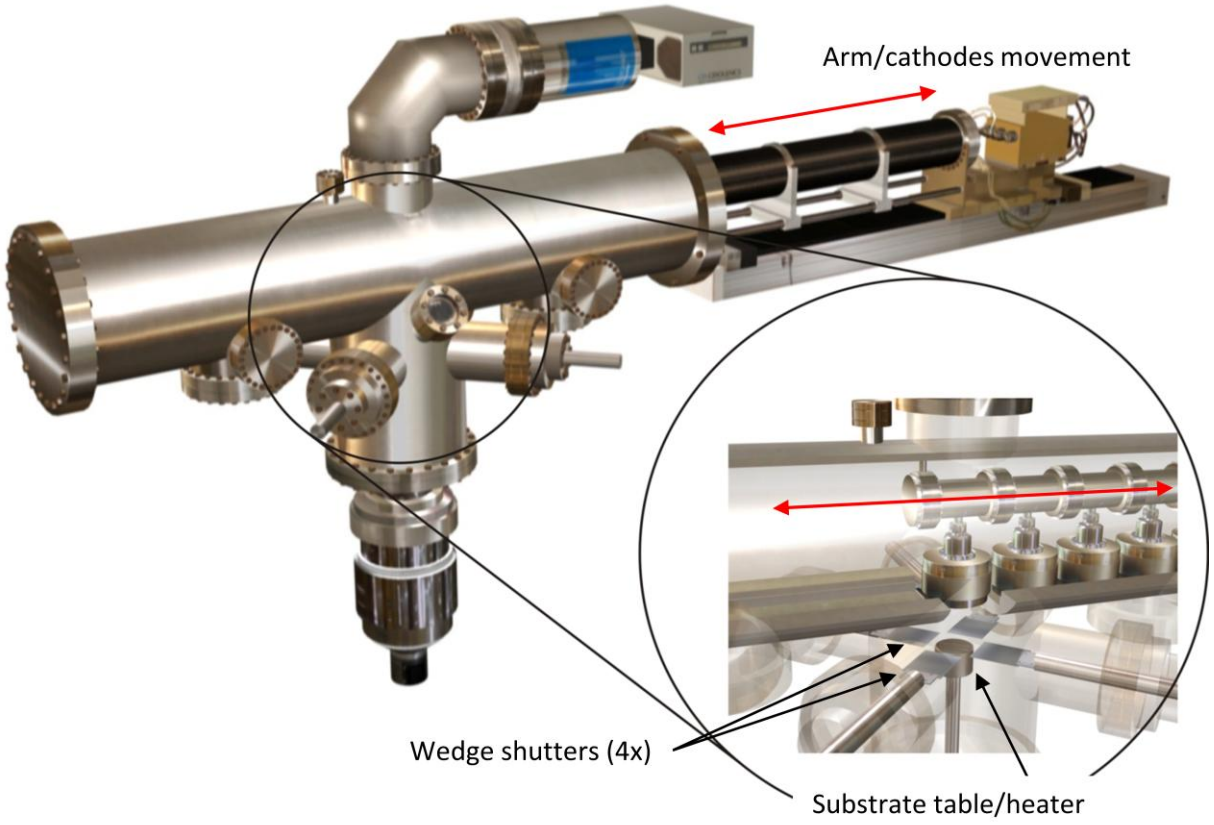


Figure 3: Drawing of a special-purpose PVD chamber for the deposition of multilayer combinatorial libraries. 6 cathodes (4 are shown in the inset cut-away diagram) are mounted to a moveable arm. Four blade-shutters can be moved to create a thickness gradient across the substrate, of material from any individual cathode. The substrate can be indexed to any rotation angle, so that a regular library can be formed (e.g. 120° rotations for each of 3 materials to form a ternary library).

Combining computer control of the deposition sources, shutter movements and substrate rotation, the full composition range from 0 at.% to 100 at.% of each constituent material can be obtained. Alternatively, the deposited range can be restricted, effectively enabling "zooming in" to make a combinatorial library having more detail within it. The constituent layers of the multilayer typically have thicknesses in the range between 1 and 10 nm and are repetitively deposited until the required total thickness, usually in the 300 to 1,000 nm range, is attained. A temperature treatment can then be used to dissolve the layers and form the final library.

If the constituent layers are elemental metals, often they are polycrystalline as deposited, but the heat treatment may lead to an amorphization reaction in some cases. An example for this is the Ni-Ti system. However the individual layers of the multilayer should be as thin as possible in order to achieve a complete mixing of the system without long annealing (diffusion) times that might favor crystallization and growth.

3.3. Deposition Profiles Shaped by Apertures

Combinatorial materials libraries have a significant advantage over one material at a time experiments in that all of the materials in the library are deposited together and therefore under the

same conditions. This removes what can be substantial confounding factors in subsequent property measurements, as the material growth conditions inevitably drift while producing an extended, systematic series of samples. In the above two methods for making combinatorial thin-film libraries, the desired library is made at one time, however only one single library is produced. When the response of the library to different post-deposition heat treatments must be determined, it is similarly useful to have multiple, identical libraries available. This was accomplished by using another type of combinatorial PVD machine[7], recently available in the *Werkstoffe der Mikrotechnik* (Materials for Microtechnology) laboratories.

In this system, a rotating main table holds up to 5 sub-tables (Figure 4). While the main table maintains a constant, simple rotation about its central axis, the sub-tables undergo additional mechanically-driven repeated forward and back 90° rotations.

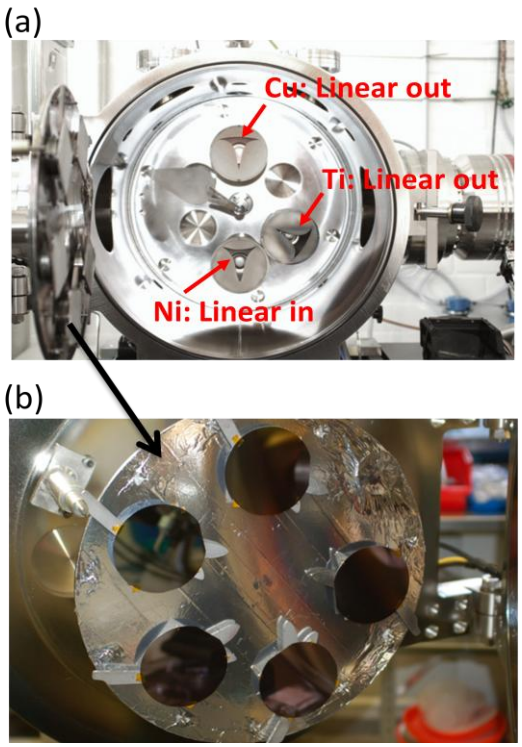


Figure 4: (a) View of chamber interior with 3 magnetron cathodes, each having a fixed aperture to shape the deposition profile to be a linear thickness wedge. The wedge may be oriented on the substrate with the thick end towards the center (linear-in) or edge (linear out) of the main table. (b) View of the main substrate table, with 5 silicon wafer substrates mounted on sub-tables. The sub-tables make repeated forward and back 90° rotations, coordinated with the main table rotation.

Figure 5 shows a diagram of the direction of the thickness wedges in relation to a substrate table (substrate), and examples of the deposition rates versus substrate location for Ti, Ni and Cu with the indicated profile-shaping apertures in place.

[7] J.R. Dahn, S. Trussler, T.D. Hatchard, A. Bonakdarpour, J.R. Mueller-Neuhaus, K.C. Hewitt and M. Fleishouer, "Economical Sputtering System to Produce Large-Size Composition-spread Libraries Having Linear and Orthogonal Stoichiometry Variations", Chem. Mater. 2002, 14, 3519 – 3523.

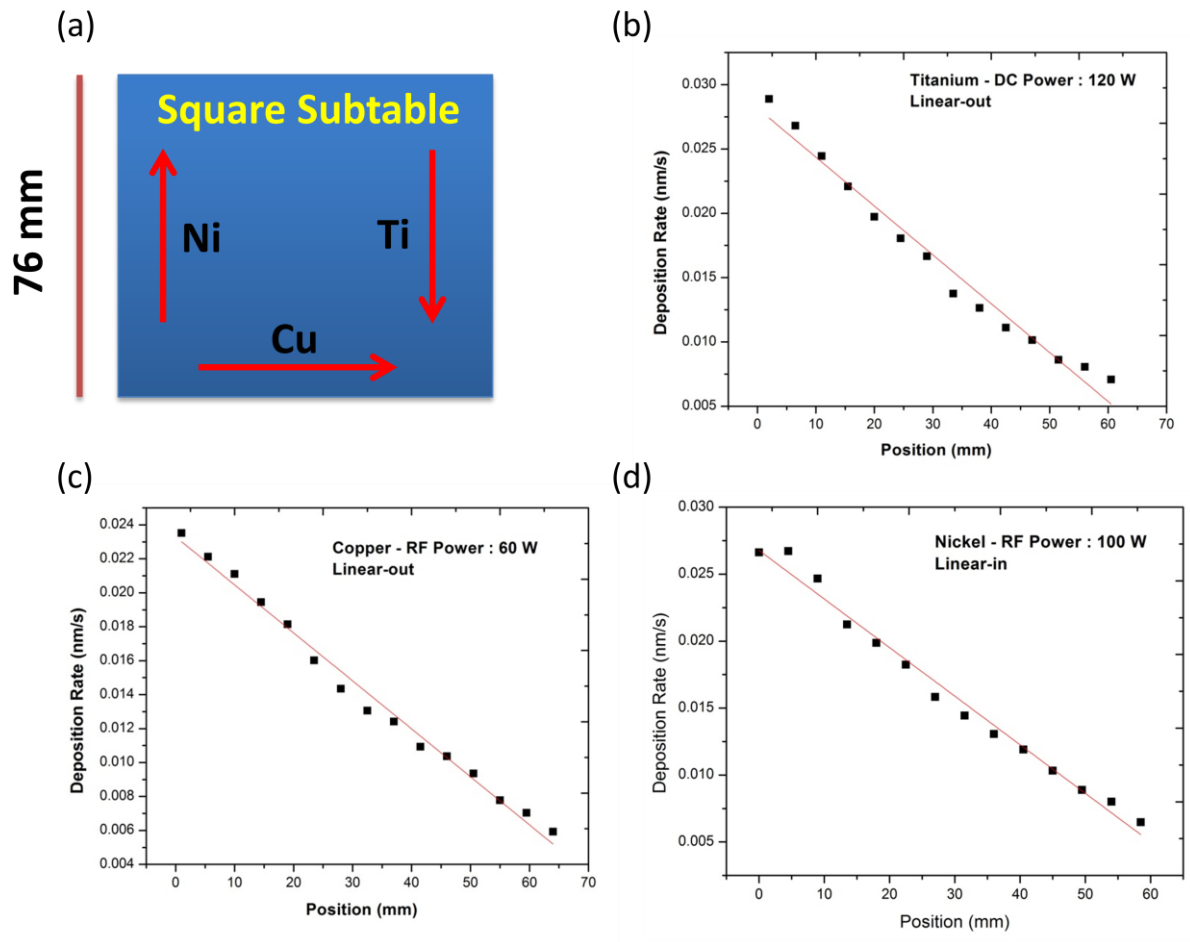


Figure 5: (a) Relative orientations of the thickness gradients for Ti, Ni and Cu for each sub-table and substrate. (b, c, d) Graphs of the individual deposition rate gradients for Ti, Ni and Cu, showing the thickness wedges for each material. Linear-in and linear-out refer to apertures attached to individual cathodes to shape the deposition rate.

The result is up to five identical combinatorial materials libraries, deposited in the same batch. Batch-to-batch reproducibility is demonstrated in Figure 6. Thus subsequent heat treatments can be carried out on entire libraries, which are directly comparable. It is considered that most of the variability seen in the figure is related to slight differences in placement and alignment of the wafers in the deposition machine and in the SEM/EDX measurement instrument, rather than coming from the depositions themselves.

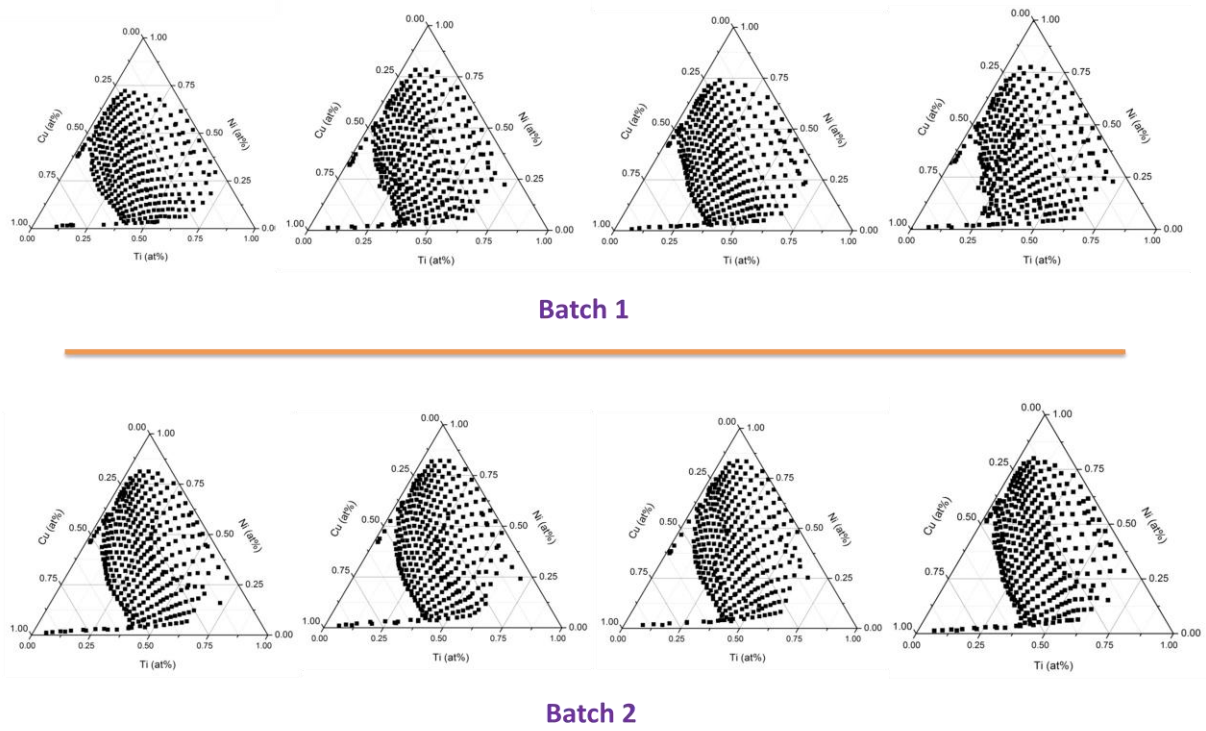


Figure 6: Maps of automated EDX data plotted as ternary composition diagrams, showing substrate-to-substrate reproducibility within a deposition batch for combinatorial Ti-Ni-Cu thin-film libraries, and the batch-to-batch reproducibility.

Table 1 presents a comparison of the capabilities of each type of PVD deposition chamber with regard to realizing combinatorial thin-film materials libraries. Because each one has unique advantages in certain situations, all may need to be employed at different points in screening for properties within complex materials systems.

Table 1: Comparison of the capabilities of different PVD machines for the making of combinatorial thin-film libraries.

Feature: / **Deposition technique:**	Complete ternary composition	Selected partial ternary	Multiple-substrate batch	Deposited film structure
Co-deposition (Section 3.1)	No	Yes	No	Atomic mixing
Sequential layers with wedge shutter (Section 3.2)	Yes	Yes	No*	Nano-multilayer
Substrate rotations + fixed apertures (Section 3.3)	No	Yes	Yes (up to 5)	Partial-layers to atomic-layers

***** Multiple, identical small libraries on a single substrate are possible, see Footnote 6.

4.0. High-Throughput Characterization Instruments

Because of the large number of different or continuously varying samples in each combinatorial materials library, high-throughput automated measurements are required for characterization. The following techniques were used in this project:

- Surface profilometry of lift-off structured substrates, for thickness mapping.
- Energy dispersive x-ray microprobe (EDX), for element composition mapping.
- Electrical resistivity (vs. location and temperature, R(T)) mapping by 4-point probe, for high-speed and high point-density materials library screening. The resistivity is correlated to thin film phase and microstructure.
- X-ray diffraction (XRD), for crystallographic analysis, or in this project, amorphous region identification.
- A method for high-throughput transmission electron microscopy (TEM) sample preparation was used.

Additionally, there are several optically-based characterization techniques being developed and applied in this project to test their suitability to detect areas/compositions that undergo amorphous to crystalline changes:

- *In-situ* measurement of micromachined cantilever bending due to film stress developed during post-deposition annealing, by monitoring the positions of reflected laser spots (see Figure 14).
- *Ex-situ* before and after heat treatment measurements by digital holography of shape changes in micromachined cantilever arrays caused by film stresses (see Figure 20).
- *In-situ* optically-monitored surface roughness, color or reflectivity changes during heat treatment, based on the change of optical properties when transforming from the amorphous to crystalline state (see Figure 26).

Each measurement or characterization technique is briefly described below, using combinatorial libraries deposited in this project as examples.

4.1. Automated Stylus Profilometry

The RUB Materials for Microtechnology laboratory is equipped with an Ambios XP2 stylus-based surface profilometer (Figure 7). This computerized, high-sensitivity surface profiler can measure roughness, waviness, and step height for a variety of applications. Step heights from under 10 nanometers to approximately 400 microns can be measured. The profiler incorporates an optical deflection height measurement mechanism and magneto-static force control system which results in a low force (loads as small as 0.05 mg) and low inertia stylus assembly. A computer-controlled x-y stage enables automated thickness mapping of patterned substrates.

Phase formation in thin films can be thickness dependent, in addition to annealing temperature and time. Because the combinatorial materials libraries are composed of thickness gradients of the individual elements, it is critical to know the total film thickness at each point on the substrate. Additionally, accurate calculation of some measured properties such as volume resistivity requires knowledge of the film thickness at each measurement point.

Figure 7: Stylus profilometer for automated mapping of deposited film thickness.

An example of such a thickness map of the library on a substrate is shown in Figure 8 (a), and, combined with automated EDX data, is re-drawn as a ternary diagram in Figure 8 (b).

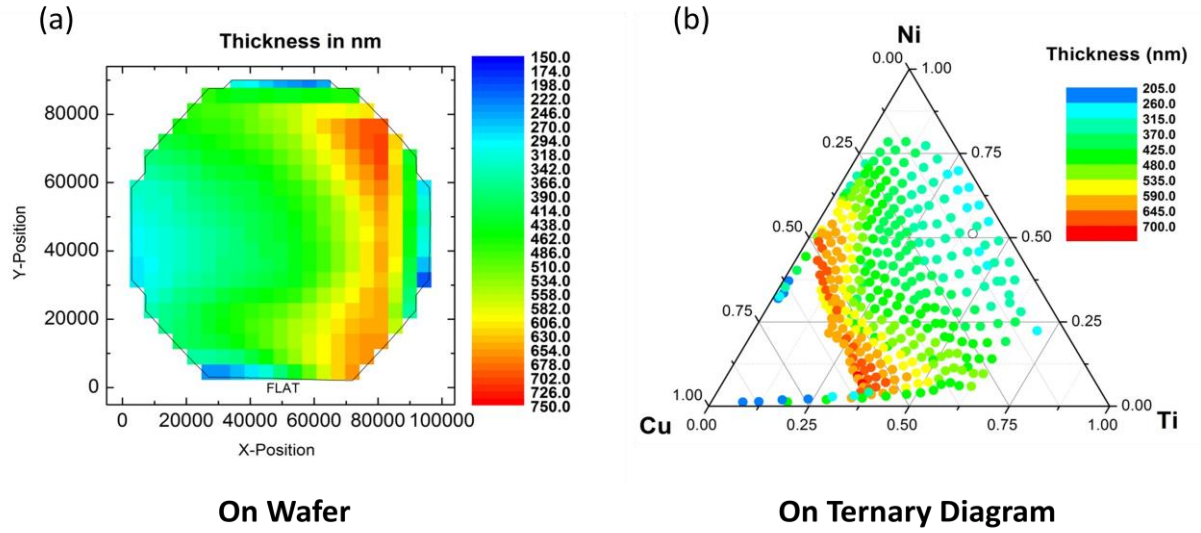


Figure 8: Thickness map of a Ti-Ni-Cu film (a) automated measurement and (b) thickness re-plotted in a ternary diagram when combined with EDX composition data.

4.2 Automated Energy Dispersive X-ray Spectroscopy Mapping

In order to determine the chemical composition across the materials library, a scanning electron microscope (SEM, JEOL 5800) equipped with an energy dispersive x-ray spectrometer (EDX) is used (Figure 9). The system employs a liquid-nitrogen-free analytical silicon drift detector (Oxford Instruments, INCA X-act), which is capable of extremely high rates of data acquisition. It can be used for qualitative or quantitative point analysis of areas of interest down to approximately 1 micrometer in diameter. Combined with an automated SEM stage, it is also used to measure line scans and element distribution maps to show the spatial distribution of elements within a combinatorial library.

Figure 9: Scanning electron microscope with automated sample stage for composition mapping by energy dispersive x-ray spectroscopy.

The Oxford analytical system consists of the EDX detector and two interface boxes (X-stream and Mics) and a standard personal computer. The EDX has an ultra-thin polymer window (200 nm) installed and can therefore detect elements from B to U. The detector is controlled from the Oxford interface, which contains the electronic hardware for the EDX signal and image acquisition, along with microscope automation hardware. The interface passes information to and receives commands from the user through the Oxford software on the computer. Image and EDX acquisition is accomplished through modular Oxford Windows software. There are four primary modules: Analyzer, Point and ID, Mapping and Automation. Qualitative x-ray identification, quantitative analysis, and x-ray mapping are available through the Analyzer module. The EDX requires a working distance of approximately 10 mm (+/- 1 mm).

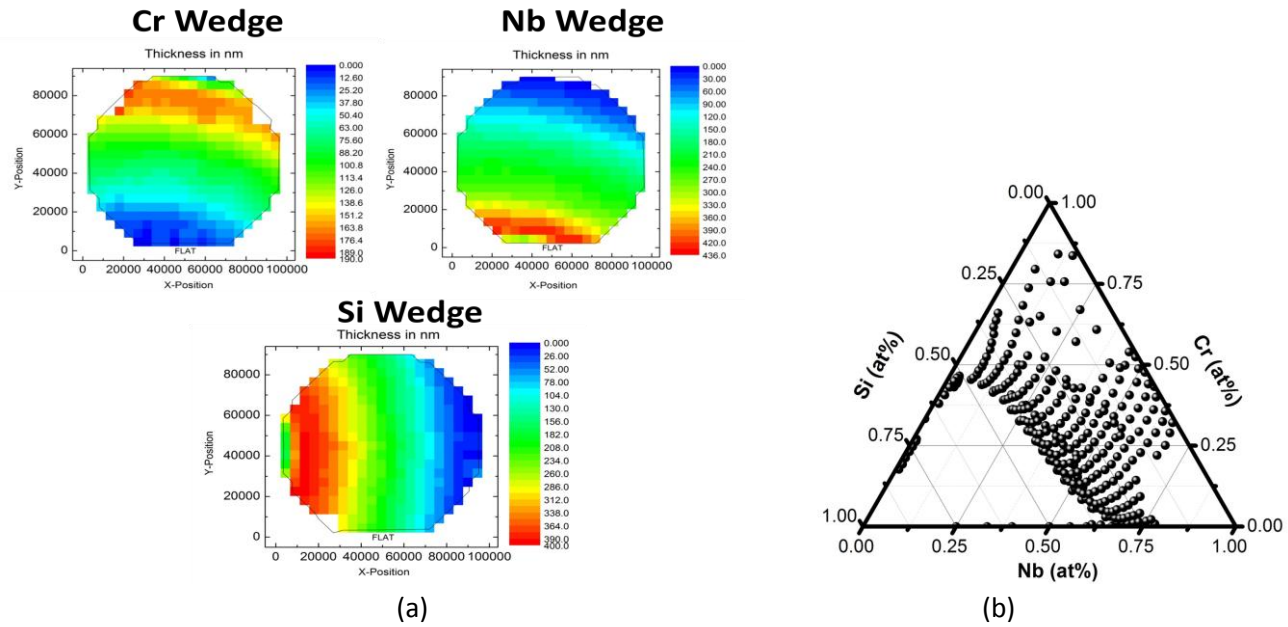


Figure 10: (a) Distribution maps of the individual elements in an Nb-Cr-Si combinatorial thin-film library, made by automated EDX. (b) Elemental distribution re-plotted in a ternary diagram.

4.3. Automated X-ray Diffraction Mapping

X-ray diffraction is generally used to characterize highly ordered crystals. It can examine nearly lattice-matched materials or the structural perfection of materials. Phase analysis of thin films and bulk samples can be performed, as well as analysis of residual stresses. The system is equipped with a detector (Panalytical PiXcel) that enables the rapid acquisition of diffraction patterns. Combined with a computer-controlled sample stage (Figure 11), it is feasible for making automated measurements of combinatorial libraries, although at a substantially slower rate than is achievable with surface profilometry or EDX.

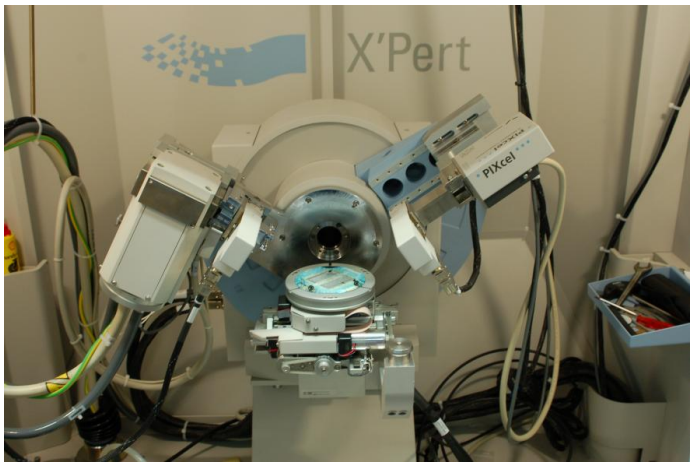
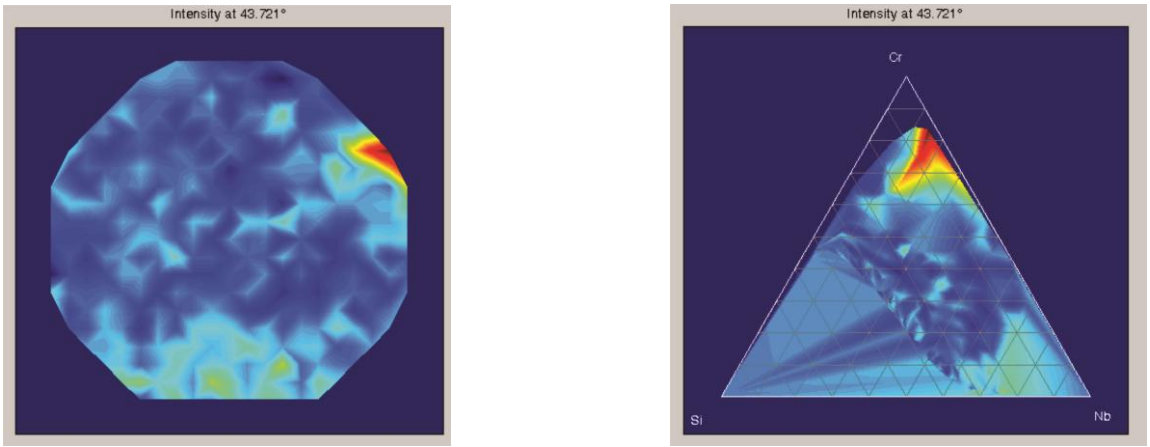


Figure 11: Micromachined 4-inch wafer mounted on the stage of the x-ray diffractometer for automated mapping.

The phase analysis of batches of combinatorial libraries can be done with this instrument. The analysis of small spots can be performed via using a microcapillary with an 800 µm diameter. In this project, the x-ray diffraction system (PANalytical X'Pert PRO) is used for high-throughput characterization, distinguishing between amorphous and polycrystalline states of the material libraries.

Figure 12 shows an example of data analysis following automated XRD scans of an Nb-Cr-Si film as-deposited on a SiO_2/Si substrate.



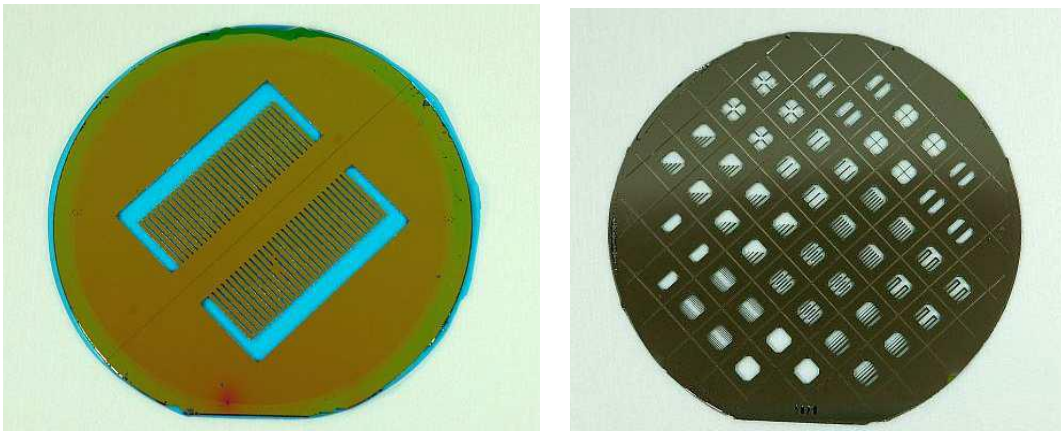
(a) (b)

Figure 12: X-ray diffraction data mapping of the Cr (110) peak in an as-deposited Nb-Cr-Si film on a SiO_2/Si substrate. (a) Wafer map of peak intensity. (b) Corresponding ternary composition diagram map. Dark red indicates the highest peak intensity, to dark blue for lowest intensity.

4.4. Optical Screening

4.4.1 Laser Deflection Detection of Cantilever bending

When amorphous compositions are identified with the above-mentioned measurements, the crystallization temperature vs. composition characteristic might be measured by monitoring the stress change in the film. To do this, a materials library is deposited on micromachined cantilevers (Figure 13), with each cantilever ideally having a unique composition, regularly varying from one cantilever to another. Changes in the film stress, for instance upon crystallization from the amorphous state, are detected by simultaneously recording the deflections of each cantilever. These deflections are measured by tracking the movement of laser spots reflected off of the cantilevers. A schematic diagram of such a measurement is shown in Figure 14, with the reflected laser spots as seen on the projection screen shown in Figure 15. In some cases, the intensity and size of the laser spots have been observed to change as well, which might later also lead to some useful correlations.



(a) (b)

Figure 13: (a) two arrays of 30 micromachined cantilevers, before thin film deposition. (b) Micromachined cantilever structures patterned wafer for digital holographic characterization.

When a materials library is deposited, each cantilever can have a unique composition. Changes in deposited film stress, for example caused by crystallization of an amorphous film, produce or change the bending of the cantilevers. Changes in each cantilever during heat treatment are measured by tracking the position and intensity of a laser spot reflected from the film surface.

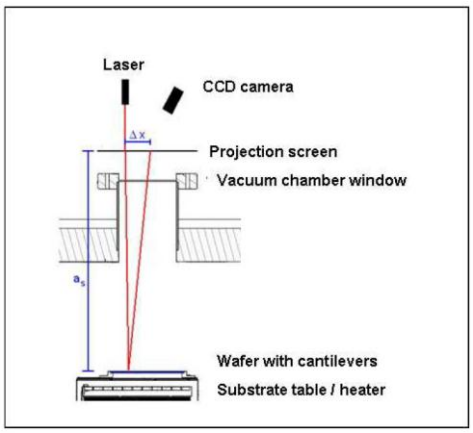


Figure 14: Schematic diagram of laser reflection measurement of cantilever bending during heat treatment.

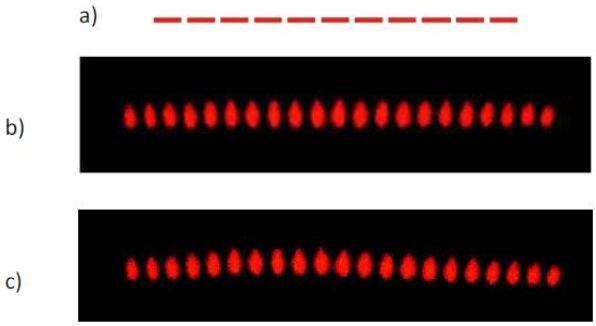


Figure 15: (a) Schematic representation of idealized laser reflections from cantilevers, b) Initial image of actual laser reflections from thin film coated cantilevers. c) Example image of laser reflections during cantilevers bending while temperature testing[8]. Because of the different coating composition on each cantilever, the response varies from one cantilever to another.

Figure 16 shows where the compositions of the materials deposited on the two sets of cantilevers seen in Figure 13(a) are located within one of the Nb-Cr-Si materials libraries created for this project. The viewport window of this proof-of-concept test platform limits the number of cantilevers that can be observed *in-situ* during heating and cooling, and therefore the number of red ("Section 1") and green ("Section 2") points are less than the full sets of 30 cantilevers each.

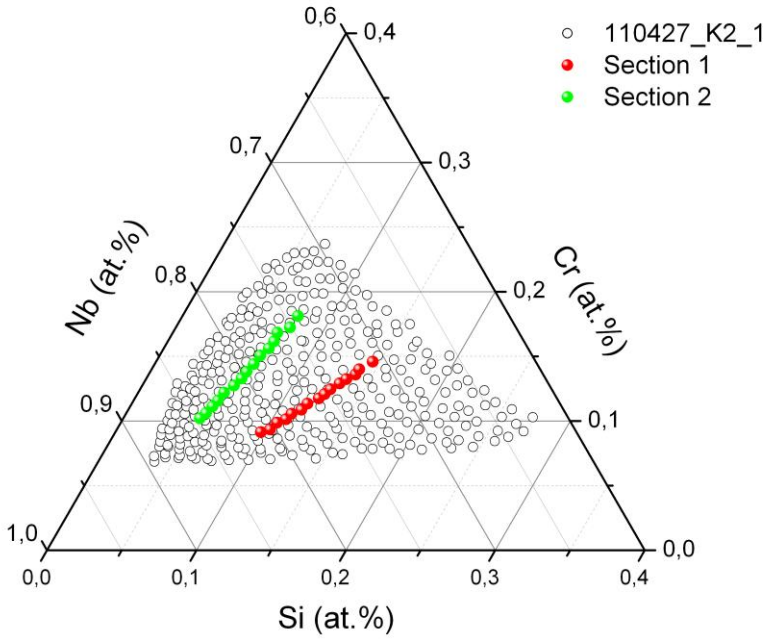


Figure 16: Compositions deposited on each cantilever, in relation to the overall materials library (open circles). Each wafer has two arrays of cantilevers: green points are the cantilevers of Section 1 and the red points are the cantilevers of Section 2.

[8] A. Siegel, Entwicklung einer optischen Messmethode zur in-situ Untersuchung von Spannungseffecten in Dünnschichtsubstratverbunden" Masters thesis, Fachhochschule Koblenz, May 2009.

The array was then heated in vacuum from room temperature to 800° C at a rate of 20° C per minute, and the deflection of 16 of the cantilevers was measured *in-situ* by laser reflection tracking (Figure 15). For clarity, only 2 cantilevers are shown. BB20 (red) had an Nb (110) XRD peak in the as-deposited state, whereas BB 4 (black) was closer to amorphous (see Figure 18). The curves begin at a deflection of -250 (arbitrary units, a.u.) and increase to a maximum at about 450° C followed by a gradual decrease in deflection as the temperature continues to rise to 800° C. The deflection change for BB 4 ("amorphous" as-deposited) is considerably larger and somewhat sharper than what is observed for BB 20 (partially polycrystalline as-deposited). For both cantilevers there was a smooth, gradual change in deflection upon cooling back to 25°C, with no observed dependence on the cooling rate.

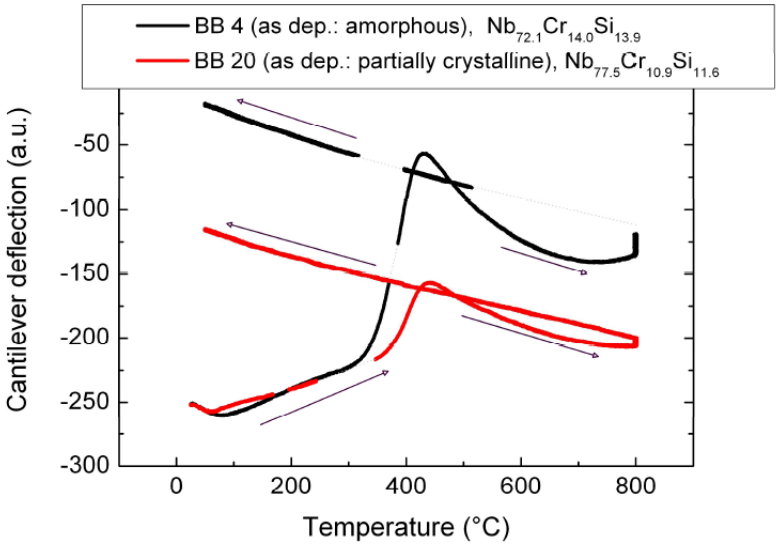


Figure 17: Cantilever deflection measured *in-situ* by laser reflection tracking. For clarity, only 2 cantilevers from the measured array are shown. BB20 (red) was partially polycrystalline in the as-deposited state, whereas BB 4 (black) was (more) amorphous. Directions of the deflection response to temperature increase and subsequent decrease are indicated by arrows.

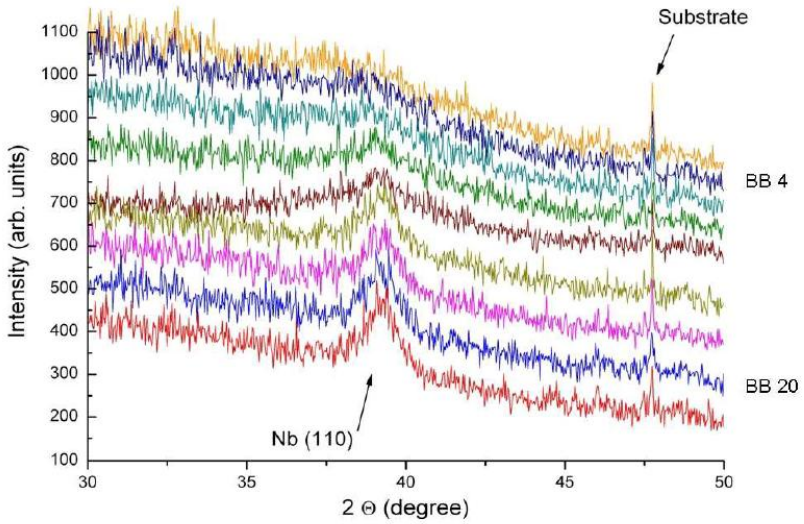


Figure 18: XRD spectra of as-deposited selected cantilevers from the Section 1 array (red points in Fig. 12). The Si substrate peak is indicated. A broad peak indexed as Nb (110) is seen at one end of the array.

XRD spectra of the annealed films on the cantilevers were then obtained again (Figure 19). The Nb (110) peak can be seen in all films on the cantilevers, although it is still very small and very broad in the cantilevers that appeared more amorphous prior to heating. A peak that can be associated with Si (220) also becomes evident after the heat treatment. It is seen that the Nb (110) peak evident in the partially polycrystalline films before heating, has neither sharpened nor intensified after heating. And although the amorphous films produced a large cantilever bending response during heating, their XRD spectra afterwards are only slightly changed. However these results are very preliminary, with considerable analysis and further experiments required for development and refinement of the characterization technique itself, so firm conclusions should not yet be drawn. A first explanation idea could be related to density changes which could occur in the films during heating.

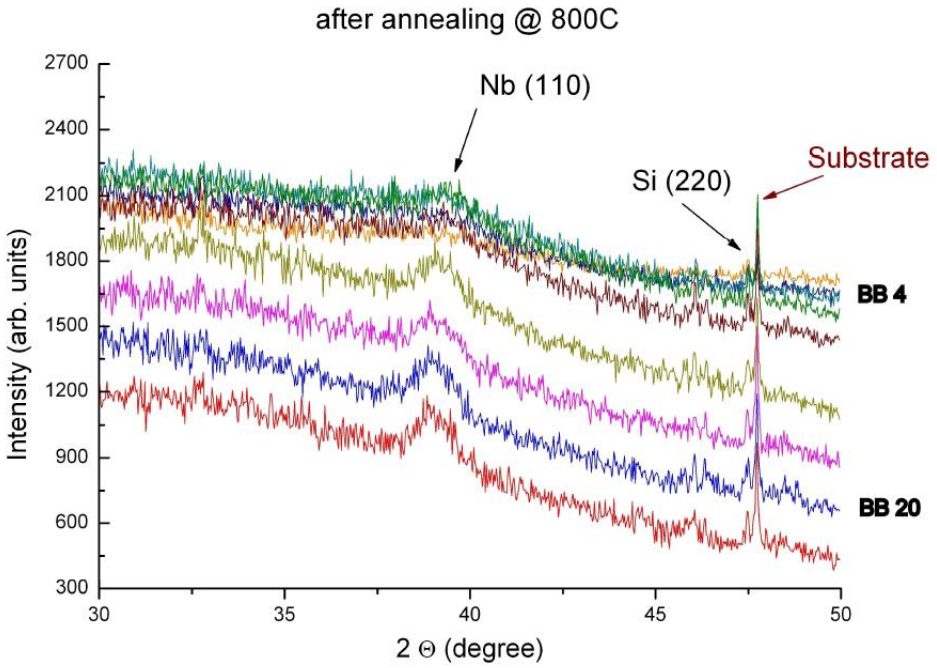


Figure 19: XRD spectra of selected cantilevers from the Section 1 array (red points in Figure 16), after heating to 800°C and cooling back to room temperature in vacuum. The substrate peak from the Si cantilevers is indicated. A broad peak indexed as Nb (110) and another peak indexed as Si (220) can be identified.

4.4.2 Digital Holographic Detection of Cantilever Bending *in-situ*

Another optically-based method of measuring shape changes in micromachined cantilever arrays caused by film stresses, density changes, etc. is with digital holography. In this technique, cantilever arrays (Figure 20) are recorded *ex-situ* before and after heat treatment, and the shape changes measured and compared.

Substrate wafers with a varied range of micromachined cantilevers of different shapes, sizes, spacing, etc. have been prepared (Figure 13b). The concept is to coat them with suitable thin films and then to thermally cycle them in order to find out if the glass forming ability matches with the density of the amorphous phase. Digital holography will be used to try to detect and measure such changes.

An example of preliminary test results is presented here. Figure 20(a) shows an overview image of cantilever array 1, physically located in a region of the wafer where it received an Nb-Cr-Si coating similar to cantilever BB20 (Figure 18 and Figure 19: partially crystalline, approximately $Nb_{77}Cr_{11}Si_{12}$). Before and after heat treatment (500°C, 10 minutes, in vacuum) shape graphs are shown in Figure 20(b) and (c) respectively. While the overall shape changes very little, the magnitude of the cantilever bending has increased significantly. (Note that the free end of the cantilever is at approximately (0, 0) in the Figure 20 graphs.)

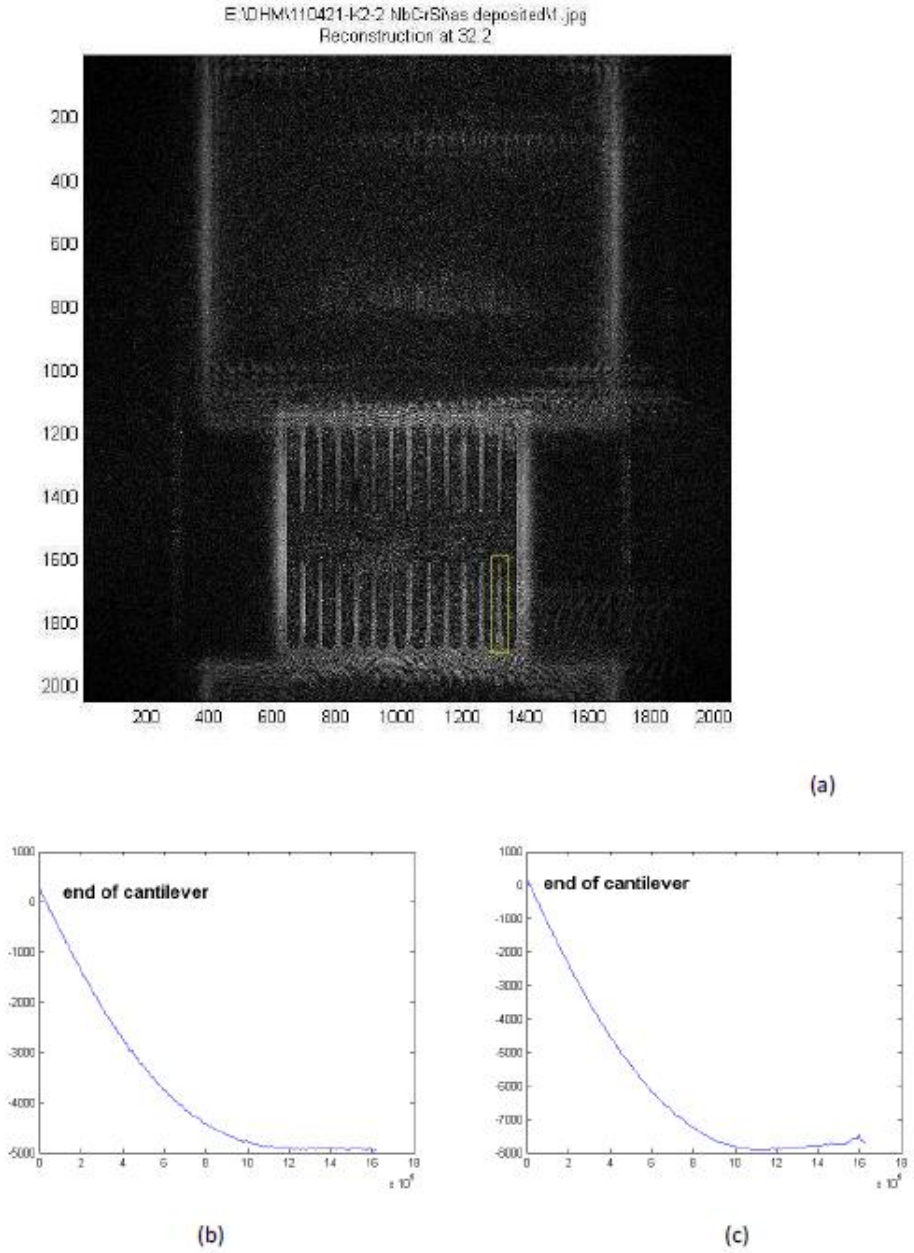


Figure 20: (a) an overview image of the cantilever array 1 with the analyzed cantilever outlined in yellow. Cantilever shape (b) before and (c) after annealing. Free end located at (0, 0).

Figure 21 (a) shows an overview image of cantilever array 29, physically located in a region of the wafer where it received an Nb-Cr-Si coating similar to cantilever BB4 (Figure 18 and Figure 19: "amorphous", approximately $Nb_{72}Cr_{14}Si_{14}$). Before and after heat treatment shape graphs are shown

in Figure 21(b) and (c) respectively, revealing that the direction of bending has reversed. (Note that in the Figure 21 graphs, the fixed end of the cantilever is at approximately (0, 0)).

While methods to analyze and interpret the digital holographic images data are still being developed, these results indicate that it may be worthwhile to continue efforts in this direction.

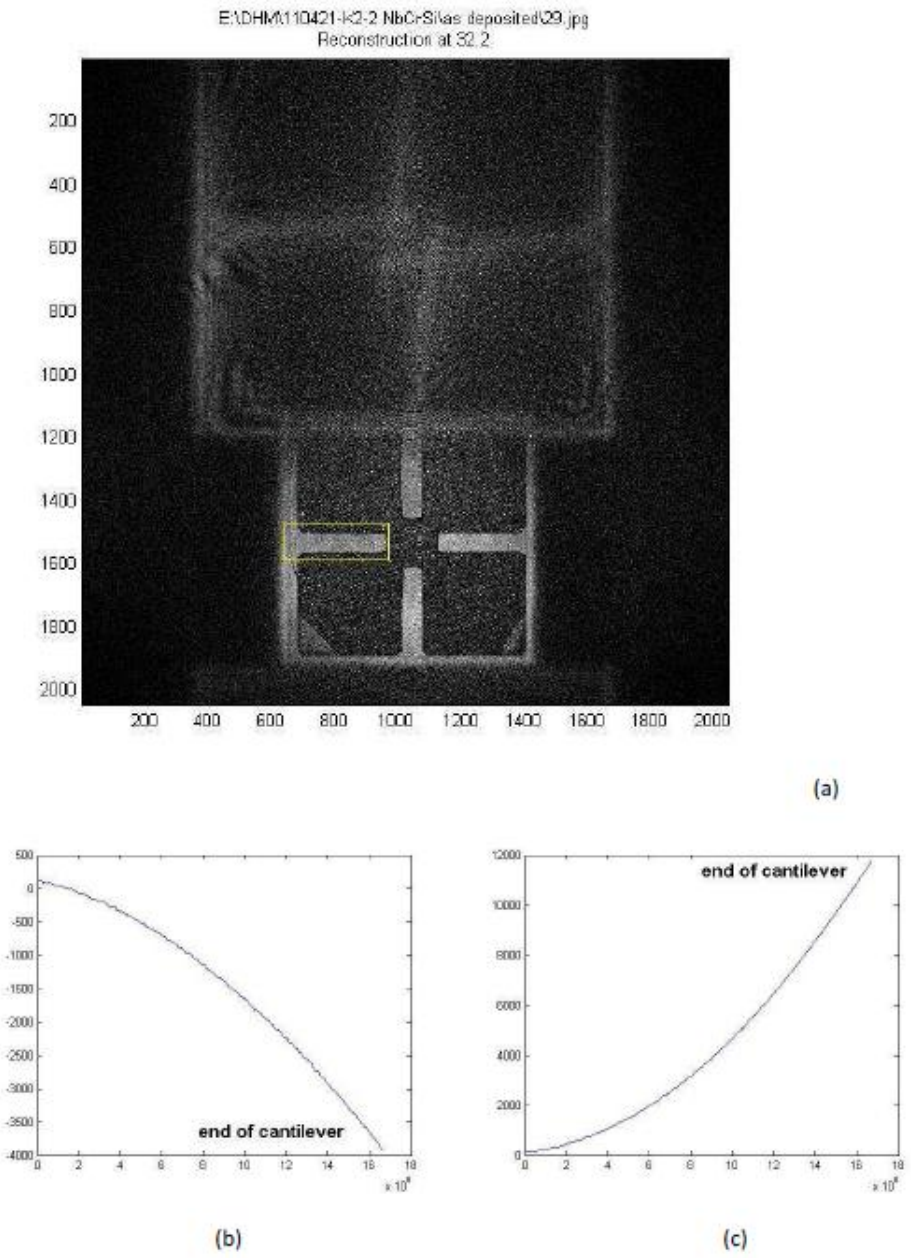


Figure 21: (a) an overview image of the cantilever array 29 with the analyzed cantilever outlined in yellow. Cantilever shape (b) before and (c) after annealing. Fixed end of cantilever located at (0, 0).

4.4.3 Digital Holographic Detection of Cantilever Bending *ex-situ*

Another *ex-situ* variation being explored is the simultaneous monitoring of a large array of micro-cantilevers over which a combinatorial thin film library is deposited. A custom-designed digital holographic microscope (DHM) captures the thin film thickness, surface topography and the

curvature of each of the cantilevers before and after deposition[9]. DHM analyzes the interference patterns created by a light beam scattered by an object, with a coherent reference beam (Figure 22). About 1500 cantilevers, each with lateral dimensions of 0.1 mm × 1 mm were fabricated out of 4-inch silicon-on-insulator (SOI) wafers by standard micro-electro-mechanical systems (MEMS) technologies (Figure 23).

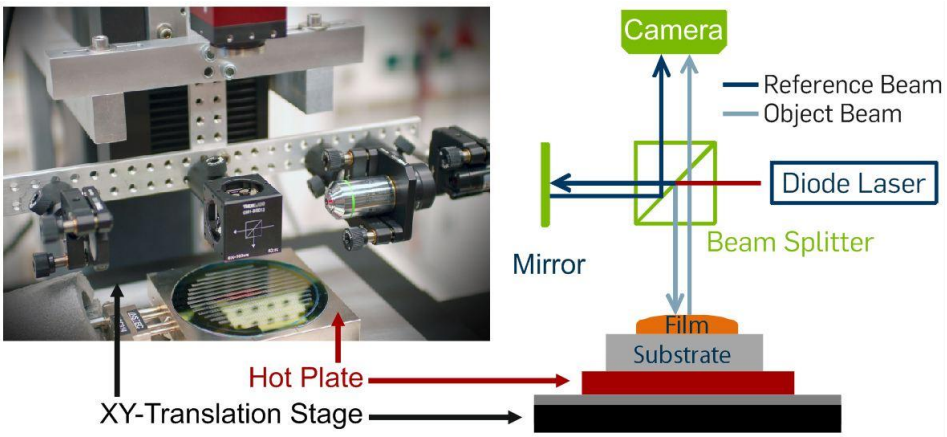


Figure 22: Digital holographic microscope (DHM) setup, showing the main components of the measurement stand.

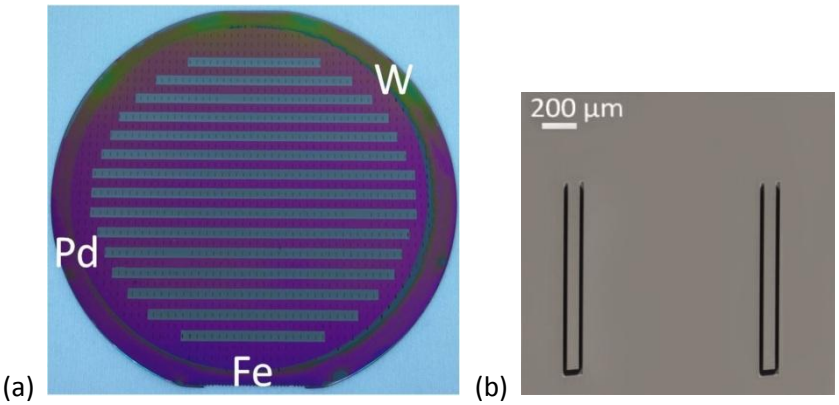


Figure 23: a) Micro-cantilever array with 1500 cantilevers, fabricated out of a SOI Wafer, coated with Fe-Pd-W materials library, b) single cantilevers of the cantilever array before deposition.

The variation in stress across the thin film materials library is then calculated using Stoney's equation based on the measured radius of curvature of each of the cantilevers and film thicknesses (Figure 24). This measurement technology is a valuable addition to the instruments available for the high-throughput investigation of stress-dependent properties (intrinsic stresses, phase formation, crystallization, etc.) in combinatorial libraries of thin films.

[9] Y.W. Lai, S. Hamann, M. Ehmann, A. Ludwig, High-throughput characterization of stresses in thin films materials libraries using Si cantilever array wafers and digital holographic microscopy, Rev. Sci. Inst. 82, 063903 (2011)

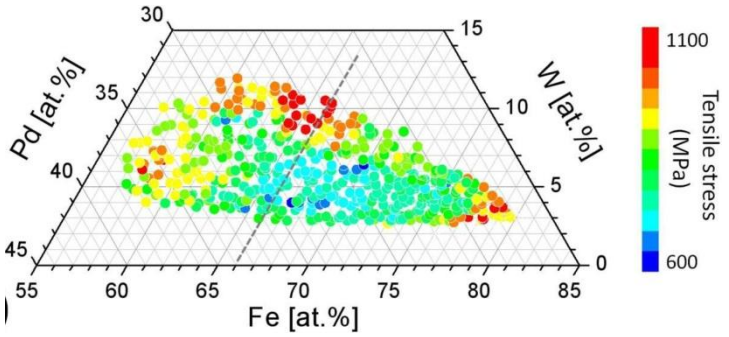
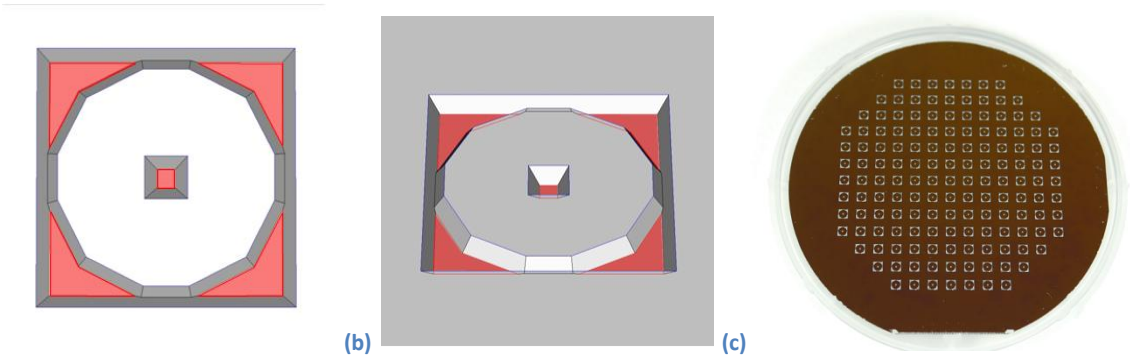


Figure 24: Tensile stress distribution in a Fe-Pd-W materials library deposited on a micro-cantilever array and measured by digital holographic microscopy.

4.5. High(er)-Throughput Transmission Electron Microscopy Sample Preparation

A technique using standard MEMS technology micromachining was developed for making an array of TEM-ready sample holders on a 4-inch diameter Si wafer. The approach taken is that an electron-beam transparent membrane is attached to a rigid micromachined Si frame (Figure 25a). These frames are themselves attached to a Si wafer, also by thin membranes (Figure 25b). The complete wafer (Figure 25c) is used for a standard thin-film combinatorial library deposition process.



(a) (b) (c)

Figure 25: (a) Top view and (b) perspective from the back side schematic drawings of a TEM-ready specimen holder, with the membrane areas indicated in red. (c) Photograph of a 4-inch wafer array of TEM-ready specimen holders ready for thin film combinatorial library deposition.

When points of interest in the library have been identified – typically from other, identical combinatorial libraries – the corresponding TEM-sample frame is simply broken out of the carrier wafer and loaded into a TEM for detailed investigation. This saves the time otherwise required to locate precisely the desired sample (composition point in the library) and then to use ion milling or grinding and polishing to cut, thin and mount it for TEM investigation.

4.6. Reflectivity/Color change

In some materials systems, it may be possible to detect microstructure changes by *in-situ* optically-monitored surface roughness or reflectivity changes during heat treatment. Figure 26 shows an example of a particular, narrow region of a complete ternary combinatorial library of Ti-Ni-Cu which changes reflectivity after transforming from the austenite to the martensite phase.

However, considerably more compositions within this full ternary Ti-Ni-Cu combinatorial library also go through this transformation, while not showing optically-visible changes. This implies that what is being detected is a surface roughness change linked to the phase change, for some particular combination of composition, thickness and/or possibly other thin film properties in this specific materials system.

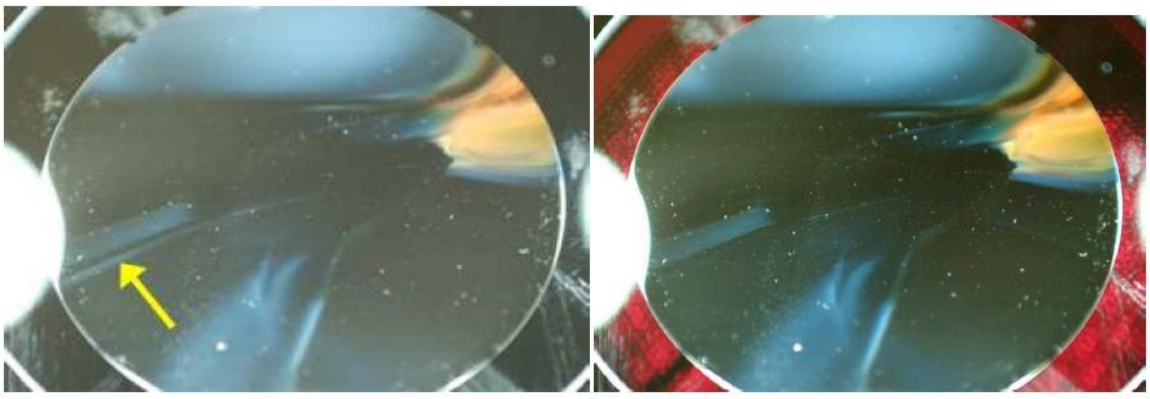


Figure 26: Optical detection of surface reflectivity changes in a complete ternary combinatorial library of Ti-Ni-Cu with temperature (a) 25°C (b) 100°C. A particular zone (indicated by an arrow) changes reflectivity, after passing through the austenite/martensite transformation temperature.

4.7. Corrosion/Oxidation Screening

First proof-of-principle results of parallel optical screening of thin-film materials libraries are shown in Figure 27. In this case, an Fe-Pd-Pt materials library was exposed to an oxygen-containing environment, with the optical surface image being recorded versus temperature. A point-by-point correlation between the image intensity, i.e. surface reflectivity, and composition was made, revealing those compositions which oxidized.

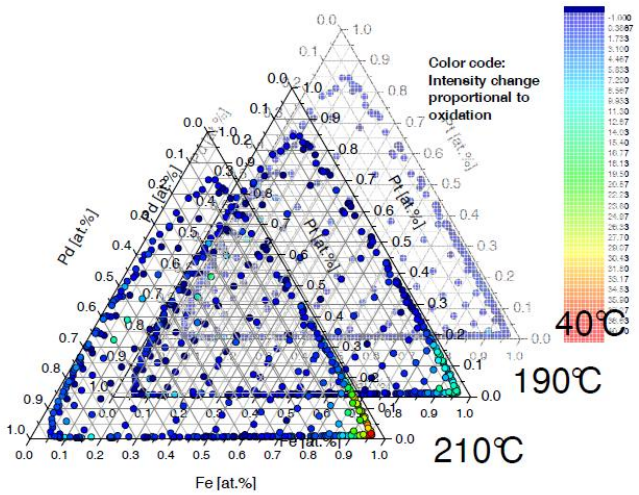


Figure 27: Results of optical parallel screening by measuring the image intensity change during oxidation plotted in ternary diagrams at different temperatures. The color code relates to intensity changes which should be proportional to oxidation.

This direct observation approach to observing the onset and progress of corrosion can be done *in-situ* over a restricted temperature range, but sufficient hardware was not available during this project to establish the working limits. However images were made in air at room temperature after defined steps of high-temperature oxidation for a selected Nb-Cr-Si library (see Figure 43).

4.8. Resistivity Change with Temperature

In-situ 4-Point Resistance Measurements Using Tungsten Needles

In order to perform resistance measurements at elevated temperature, a suitable vacuum chamber with a heater is needed. The entire interior of the chamber has to be compatible with the high temperatures to which it will or could be exposed. This is not trivial because many materials tend to change their structure and properties, and some will outgas from their interior volume when heated. The goal is to set up a chamber which is suited for high-throughput resistance measurements at temperatures above 600°C. For the first experiments, we had to use a chamber which was not ideal for this, but was immediately available and which could serve as a test bed for materials and construction techniques.

Experiments were performed using a high vacuum chamber (base vacuum $1x10^{-6}$ mbar) which has a heater with a maximum temperature of 600°C. Only samples with a maximum size of 50mm x 10mm could be annealed with this heater. We built a resistance probe head from Macor (a machinable ceramic) which holds 12 tungsten needles (i.e. 3 sets of 4-point resistivity measurement probes) which were fixed in place with special high temperature ceramic glue (Figure 28). The pins were arranged in groups of four to perform 4-point resistance measurements. The cables were clamped and glued to the pins and isolated with high-temperature tubing made from silica. With this arrangement, three samples can be measured together under vacuum (serial measurements), with each probe set passing through a switching matrix to a high-precision source meter (Model 2400 digital source meter, Keithley Instruments). In an advanced setup, the number of pins will be increased to up to one hundred or more.

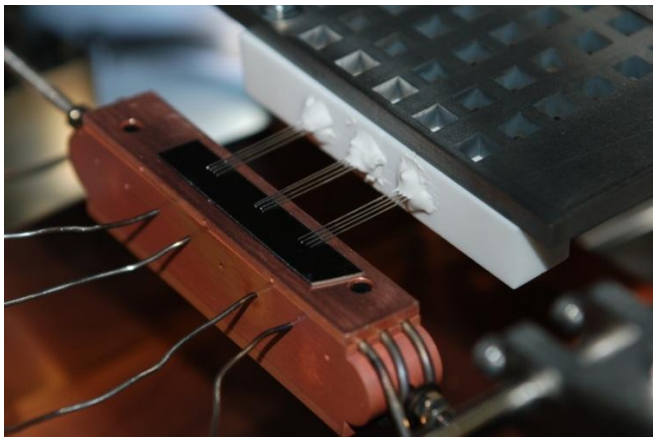


Figure 28: Photo of a sample positioned on the heater inside the vacuum chamber. 12 tungsten needles in groups of four are contacting the sample for 4-point resistance measurements. Also shown are the thermocouples inserted into the copper block of the heater.

Tests were performed with samples from a Ti-Ni-Cu materials library, in vacuum without inert gas atmosphere because the chamber available had no water cooling. Inert gas would be preferred for better temperature uniformity, but for this effective water cooling is essential. The temperature was

measured using thermocouples inside the copper block of the heater. Since the sample was positioned on this block, there was a temperature offset between the measured and the real sample temperature. The exact offset could not be determined during these first experiments.

During the annealing to 600°C, the chamber pressure rose to $4x10^{-4}$ mbar due to outgassing of the various materials inside the chamber. With this setup, programmable temperature control has not been implemented, so we were not able to heat with a controlled rate. Therefore the heating rates varied, with a maximum of 30°C/min. Since there was likewise no active cooling installed, the heater was just turned off for cooling. After annealing, the samples looked darker, most likely due to oxidation.

Even though the setup was not ideal, these first measurements looked promising and showed measurement curves having indications of the onset of crystallization of the samples. The crystallization is expected to take place at the temperature where a kink in the R(T) curve appears (Figure 29). A second run carried out with the same samples (not shown here) showed only a linear curve without transformation, suggesting that the most readily crystallized material had transformed, although at this time it is difficult to correlate with XRD data from the same locations. Samples which were already crystallized in the as-deposited state did not show this kink. Across a 50 mm sample of a Ti-Ni-Cu materials library, the indicated crystallization temperature varied by about 30°C.

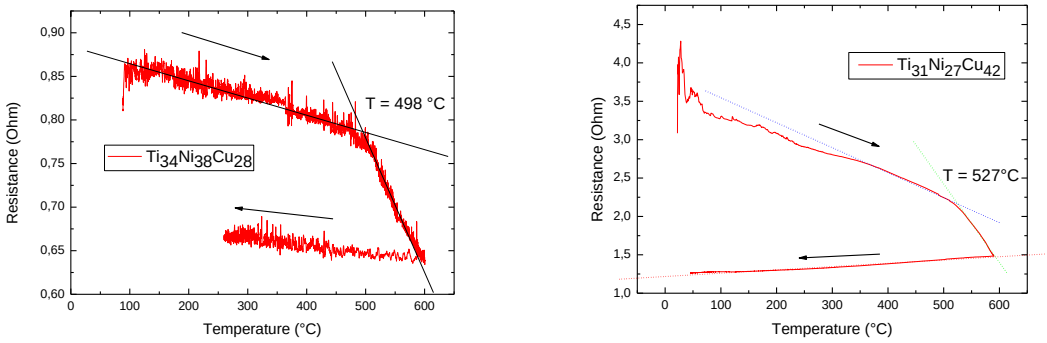


Figure 29: R(T)-curves show a kink at a temperature of 498°C and 527°C respectively, which is ascribed to the onset of crystallization of the as-deposited amorphous samples.

This may be compared with an earlier investigation of structural transformations, where micro-hotplates were coated with $Ni_{30}Ti_{55}Cu_{15}$ thin films of approximately 500 nm thickness. This alloy is a well-known conventional shape memory alloy (SMA) that undergoes a martensitic transformation after appropriate heat treatment[10]. The Ni-Ti-Cu thin films were deposited from an alloy target onto micro-hotplate substrates. The film was then annealed to crystallize the amorphous SMA thin film (Figure 30). The annealing conditions were a heating rate of 1.67 K/s to a final temperature of 875K, held for 10 seconds. The electrical resistivity decreased gradually with increasing temperature, then fell rapidly at 689 K. The sudden drop in resistivity stopped at 717K, then increased with increasing temperature.

[10] K. Otsuka, Shape Memory Materials, Cambridge University Press, 1998, pp. 184–219.

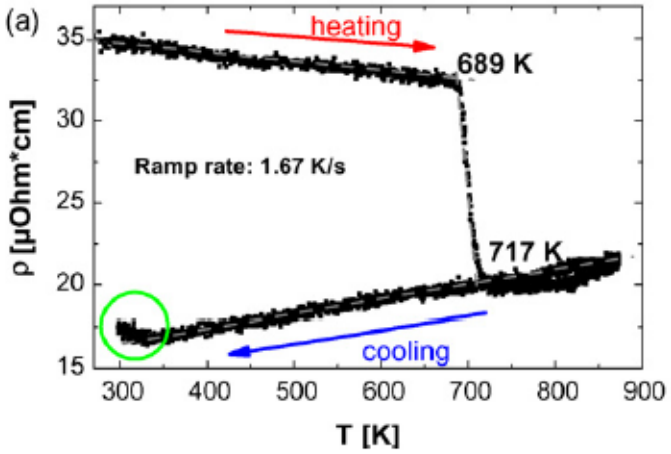


Figure 30: Resistance-temperature behavior of an as-deposited $Ni_{30}Ti_{55}Cu_{15}$ thin film upon first annealing. Reproduced from [11]

The change in temperature where the amorphous to crystalline transition occurred can be attributed to the different elemental compositions, film thickness, and possibly to the very different heating rates for the two experiments.

For the future, a water-cooled vacuum chamber is needed which offers sufficient space to place a full 4" wafer inside, plus all the cabling that is needed for a high-throughput measurement setup of 10's to 100's of 4-point probe sets. Inert gas with high purity should be used during the annealing. Although there was insufficient funding to purchase or build up a complete test stand at this time, some of the critical components to set up such a chamber have been purchased by the funding of this project.

4.9. High-Temperature Characterization Test Stand

A design study of a testing and measurement test stand was undertaken, to build up an instrument which can flexibly incorporate as many as possible of the methods outlined in the preceding section over a wide range of temperature, pressure and gas environment conditions.

[11] S. Hamann, M. Ehmann, S. Thienhaus, A. Savan, A. Ludwig, Micro-hotplates for high-throughput thin film processing and in situ phase transformation characterization, Sensors and Actuators, A 147 (2008) 576 – 582.

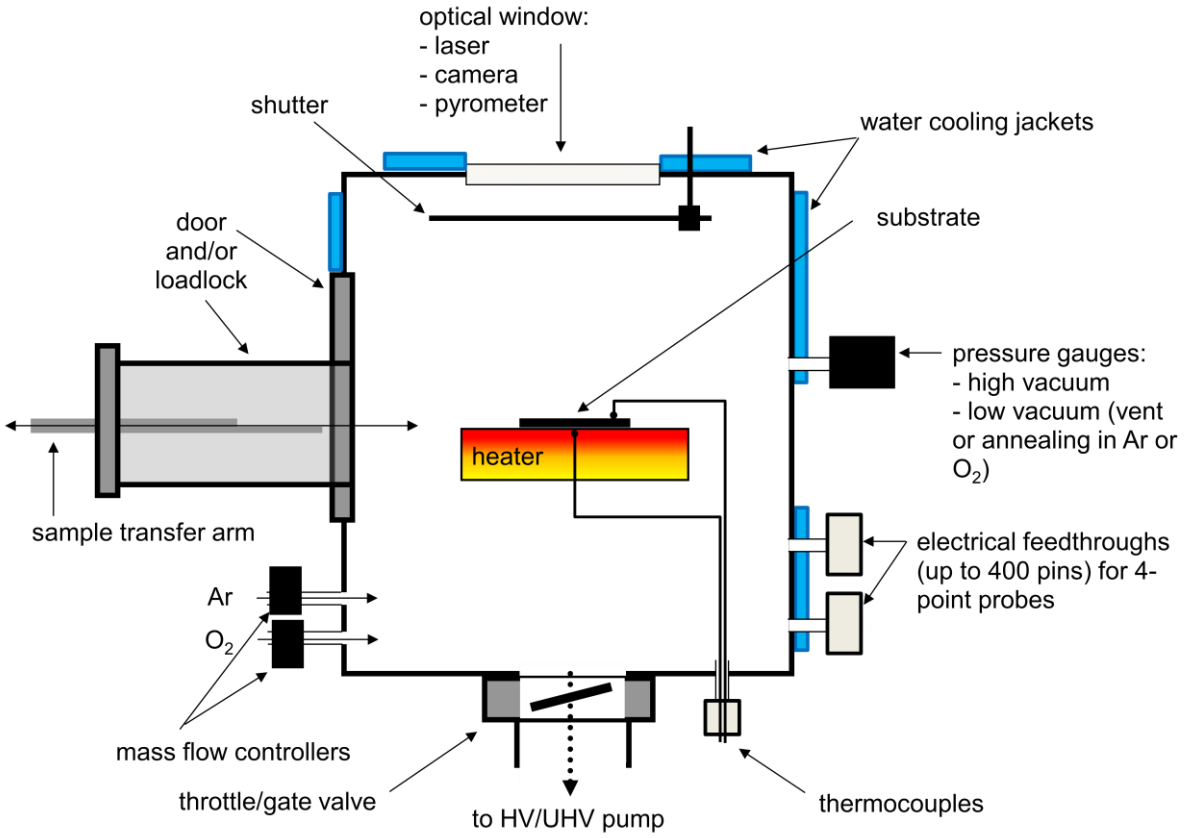


Figure 31: Schematic diagram showing the major elements of an integrated high-temperature heat treatment and corrosion study test instrument.

Commercial suppliers of high-temperature, vacuum furnaces surveyed did not have any standard product able to provide or feasibly be adapted to provide the range of features and performance envisioned for a testing chamber capable to fulfill the aims of this project. This was the case even if the requirement for a loadlock and transfer mechanism was relaxed. However without a loadlock, excessive pumping times would be required to prevent oxidation during high-temperature annealing, with few possibilities for increasing the outgassing/desorption rate of the chamber and contents prior to annealing.

An industrial equipment supplier was able to offer a modified PVD chamber equipped with a loadlock and the other required hardware features (indicated in Figure 31). However the cost was considerably above the budget available for this project. Therefore a study was made into the feasibility of purchasing the needed components and building up a high-temperature test and measurement instrument using resources available in the *Werkstoffe der Mikrotechnik* department.

Figure 32 shows sketches of the “standard” chamber designs that were considered. While a spherical chamber (Figure 32 (a)) is the most attractive from the standpoint of measurement placement and flexibility, both it and Figure 32 (b) were eventually rejected because of the difficulty in adequately cooling flanges with windows or electrical feedthroughs. (There is interest in using such a high-temperature test stand also for materials such as superalloys where the temperature may need to be in the range of 1400 °C.) So finally the most feasible and cost-effective chamber design would be cylindrical, with separately cooled sides and ends.

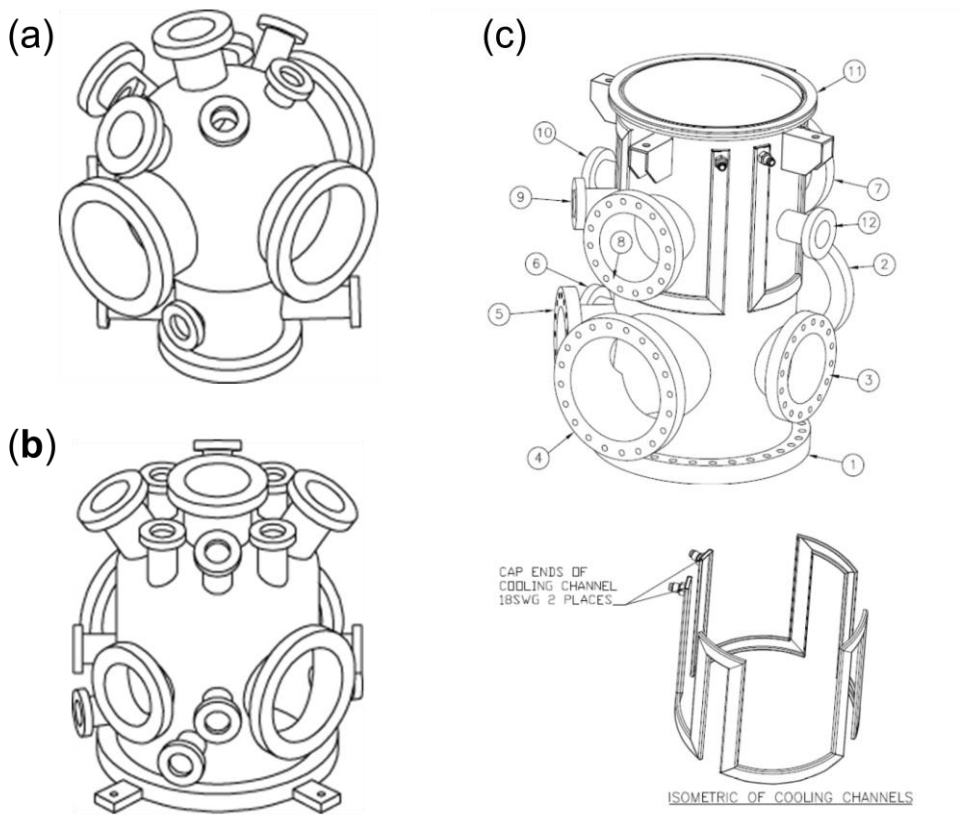


Figure 32: Multipurpose UHV testing and measurement chamber design study examples: (a) spherical, (b) cylindrical with open flanged end and closed dished end, (c) cylindrical with open flanged ends and cooling channels.

While there are not sufficient funds presently available to build up a full test stand that incorporates all of the desired features and performance ranges, several of the most critical components have been acquired so that we can fabricate and develop parts of the instrument using chambers and heaters that are currently available, until sufficient funding is available to construct a full instrument.

5.0. Application to Investigation of Amorphous Metal Compositions

The deposition techniques described in Sections 3.1, 3.2 and 3.3 were used to make combinatorial thin film libraries of Ti-Ni-Cu and Nb-Cr-Si. These libraries were then characterized before, during and after annealing with high-throughput characterization instruments as applicable to the case, with regard to identifying amorphous regions within the libraries and their temperature stability ranges.

5.1. Ti-Ni-Cu

Two sets of identical combinatorial libraries of Ti-Ni-Cu were deposited using the aperture-shaped deposition technique described previously (Section 3.3). One of these libraries was set aside to be the as-deposited reference, while 5 others were separately annealed in ultra high vacuum (UHV) at 300°, 400°, 500°, 600° and 700°C respectively, each for 1 hour with a 50°C/minute heating rate. Automated high-throughput XRD mapping was used to characterize each library.

The intention of this experiment was to identify amorphous and crystalline regions in the as-deposited library, and then to track the changes in these areas after the various subsequent annealing treatments. However distinguishing between truly amorphous versus partially crystallized

or very fine-grained/nano-crystalline versus polycrystalline materials, based on XRD spectra is ambiguous due to the possible presence of an amorphous "peak" (or "hump"), and very small peaks that may be noise or may gradually grow to be crystallographically-identifiable peaks either from phases or precipitates being formed. Thus, a simple classification scheme was implemented based on the normalized (i.e. background subtracted) XRD intensity:

I < 50 counts + broad peak with no small peaks ➡ amorphous
I < 50 counts+ broad peak with small peaks ➡ amorphous, partially crystalline or crystalline (with very small grain size)
I > 50 counts ➡ partially crystalline or crystalline

Figure 33 shows such a map of the as-deposited Ti-Ni-Cu library, with representative examples of the spectra acquired for the classification scheme above: crystalline/partially crystalline (Sample A), amorphous but near the boundary with crystalline (Sample B), and amorphous (Sample C) regions.

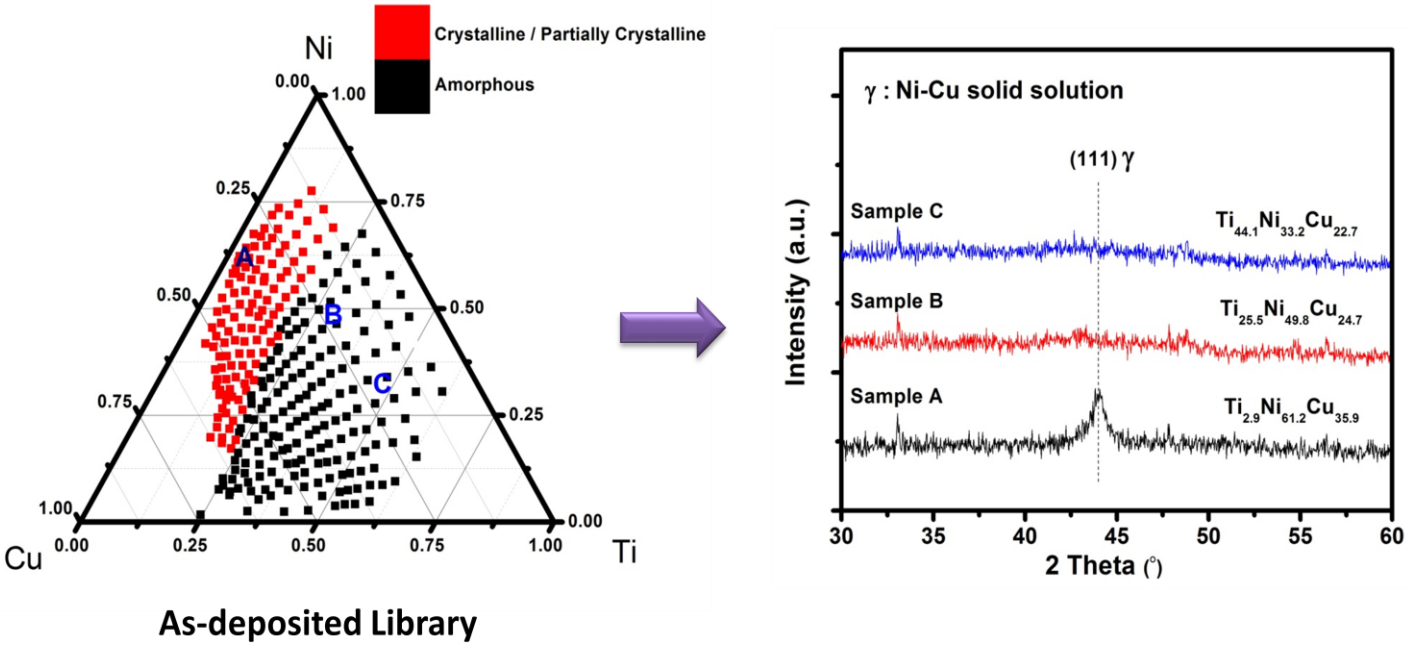
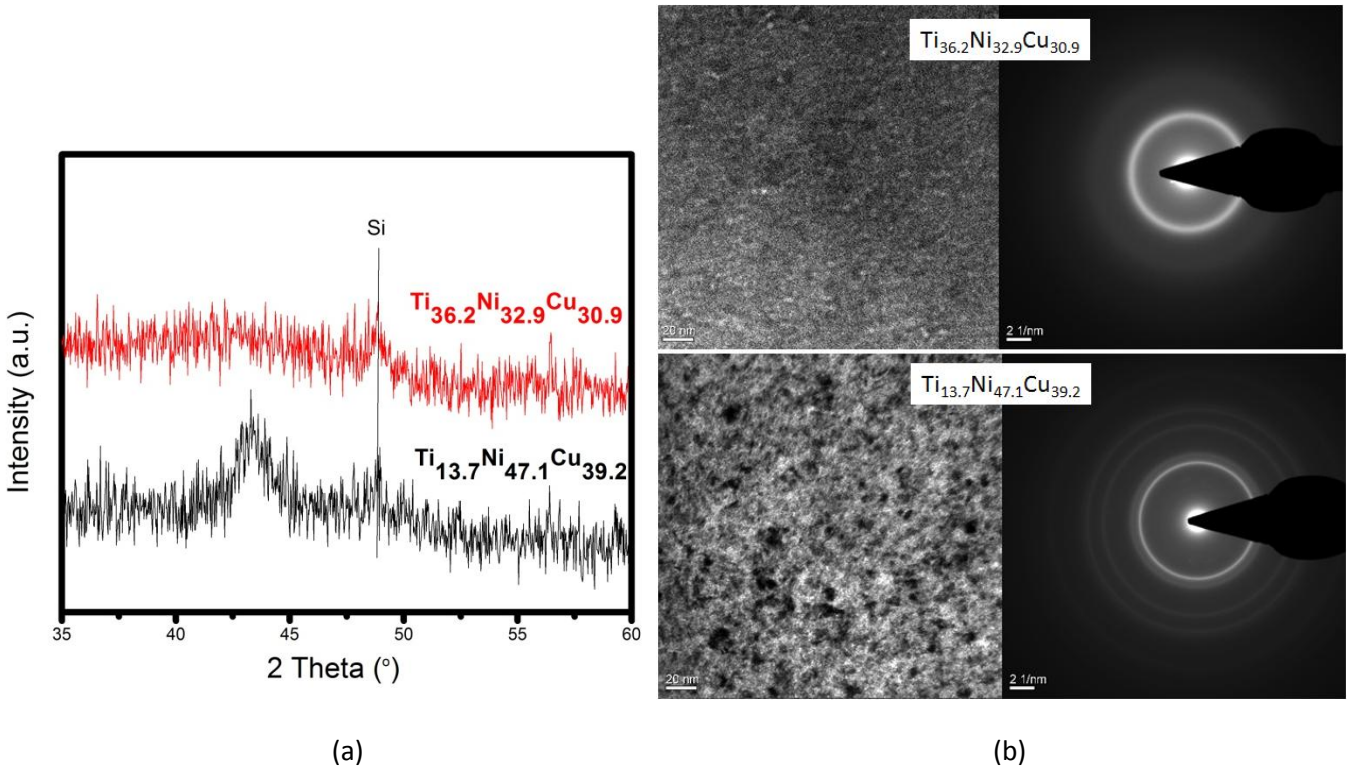


Figure 33: XRD structural analysis of amorphous and crystalline/partially crystalline regions of an as-deposited Ti-Ni-Cu combinatorial thin film library. Classification scheme is described in the text.

Ultimately, TEM is required to clarify the preliminary interpretations of the XRD spectra, and to verify the categorizations that were made. While TEM cannot be considered as a high-throughput materials analysis technique, a higher throughput method of TEM sample preparation is being developed (Section 4.5), and was applied and tested as part of this project.

A consequence of the elemental concentration wedge technique for depositing combinatorial thin film libraries is that the total film thickness is not uniform (see Figure 8, where the total film thickness of the Ti-Ni-Cu library varies from about 250 nm to 750 nm). Some film properties, microstructures and behavior are thickness dependent, yet TEM imaging requires a sample thickness of less than 300 nm. Therefore, a Ti-Ni-Cu library was deposited on the micromachined TEM-sample substrate using identical process conditions as used for the other libraries, with only a shorter deposition time and thus lower thickness.

Figure 34(a) shows XRD spectra tentatively classified as amorphous (red: $Ti_{36.2}Ni_{32.9}Cu_{30.9}$) and as partially crystalline/crystalline (black: $Ti_{13.7}Ni_{47.1}Cu_{39.2}$). TEM images and selected area diffraction patterns for identical compositions, shown in Figure 34(b), tend to support the classification criteria that were chosen, i.e. normalized (background subtracted) spectra having a low intensity, broad peak and no small peaks being amorphous, and spectra having higher intensity, small peaks being partially crystalline or crystalline.



(a) (b)

Figure 34: a) XRD spectra from points in a TiNiCu combinatorial library considered as amorphous (red) and crystalline/partially crystalline (black). b) TEM images and selected area diffraction patterns from the corresponding compositions.

This possible methodology for rapid screening of materials libraries is being further investigated and refined with guidelines and boundaries for applicability. However it is a step in the direction towards developing high-throughput screening methods for large combinatorial materials libraries.

Using identical as-deposited combinatorial libraries (deposited continuously in the same batch), a series of temperature treatments were done in ultra-high vacuum (UHV, base vacuum approximately $2x10^{-8}$ Torr). In each case the wafer being annealed was heated from room temperature to the designated annealing temperature at a rate of 50°C/minute and held there for 1 hour, with subsequent cooling at the maximum natural rate. The same classification methodology was used to map changes in crystallinity as measured by automated XRD (Figure 35).

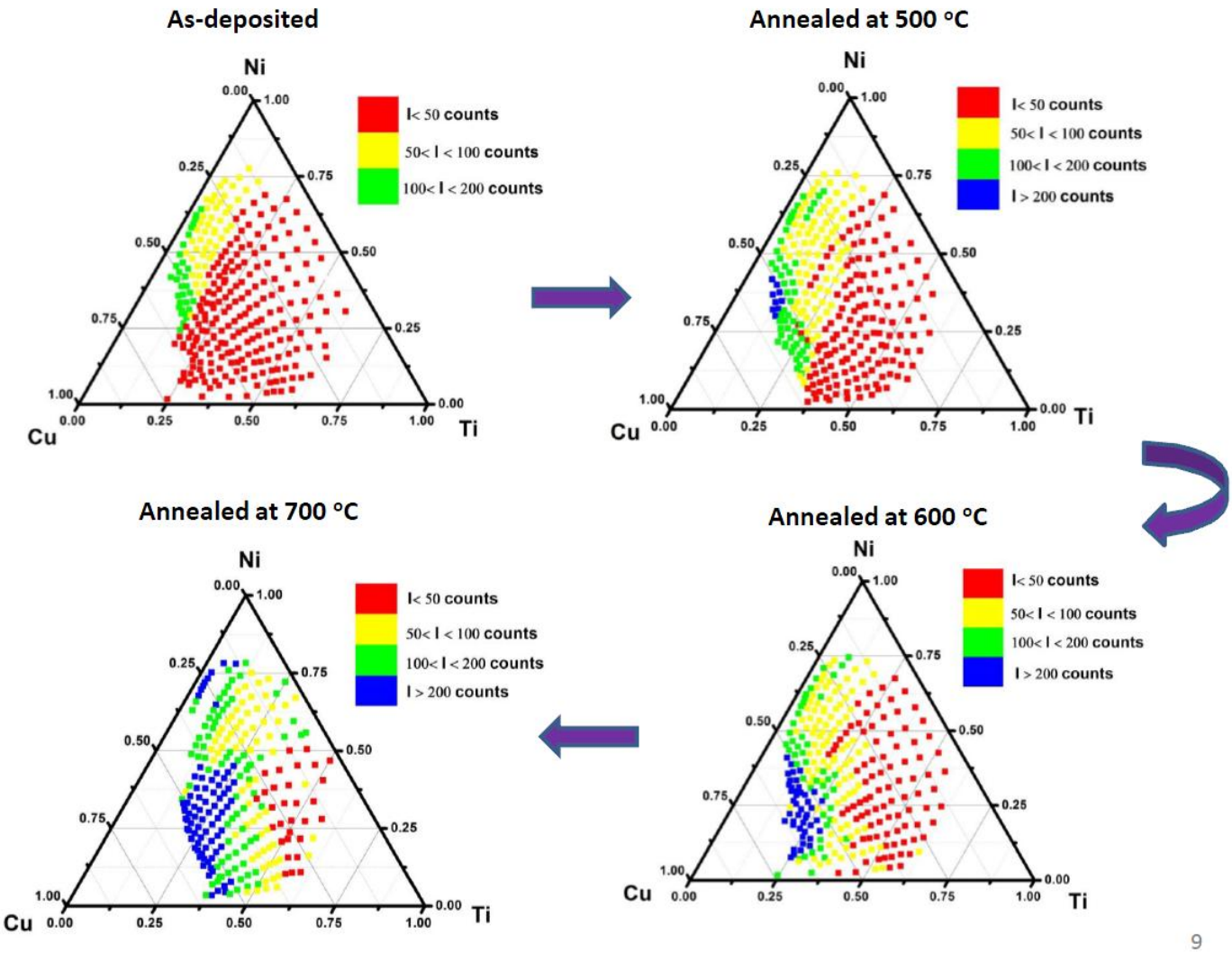


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Figure 35: Crystallization behavior measured by XRD for 4 identical Ti-Ni-Cu combinatorial libraries, as-deposited and following 1 hour annealing in UHV. The normalized XRD count intensity for the highest film peak, if any, is plotted on a color-coded scale in the ternary composition diagram.

The Ti-Ni-Cu materials system has been well characterized, with regard to discovery and understanding of the composition regions undergoing the reversible martensite to austenite microstructure transformation, i.e. shape memory alloys[12]. However typically the compositions which do not show shape memory properties are not further studied. The response of Ti-Ni-Cu alloys to thermal treatments is complex in terms of phases, solid solutions and precipitates, and even more so in the case of thin films where PVD can result in metastable phases and crystallization behavior can be additionally influenced by thickness[13].

[12] R. Zarnetta, M. Ehmann, A. Savan, A. Ludwig, Identification of optimized Ti-Ni-Cu shape memory alloy compositions for thin film microactuator applications, Smart Mater. Struct. 19 065032, 2010.

[13] X. Wang, M. Rein, J. J. Vlassak, Crystallization kinetics of amorphous equiatomic NiTi thin films: Effect of film thickness, Journal of Applied Physics 103, 023501 ,2008.

While detailed investigation of the crystallized films is beyond the scope of this project, some selected points of the library were analyzed in more detail as a demonstration of the ability to pick out and study compositions identified to be of interest (Figure 36). Automated XRD measurements are implemented in the *Werkstoffe der Mikrotechnik* laboratory in an instrument with a sensitive, high-speed detector, which can acquire an individual spectrum in approximately 8 minutes. Thus, mapping of a combinatorial library on a 4-inch circular substrate with a resolution close to the minimum x-ray spot size requires about 15 hours.

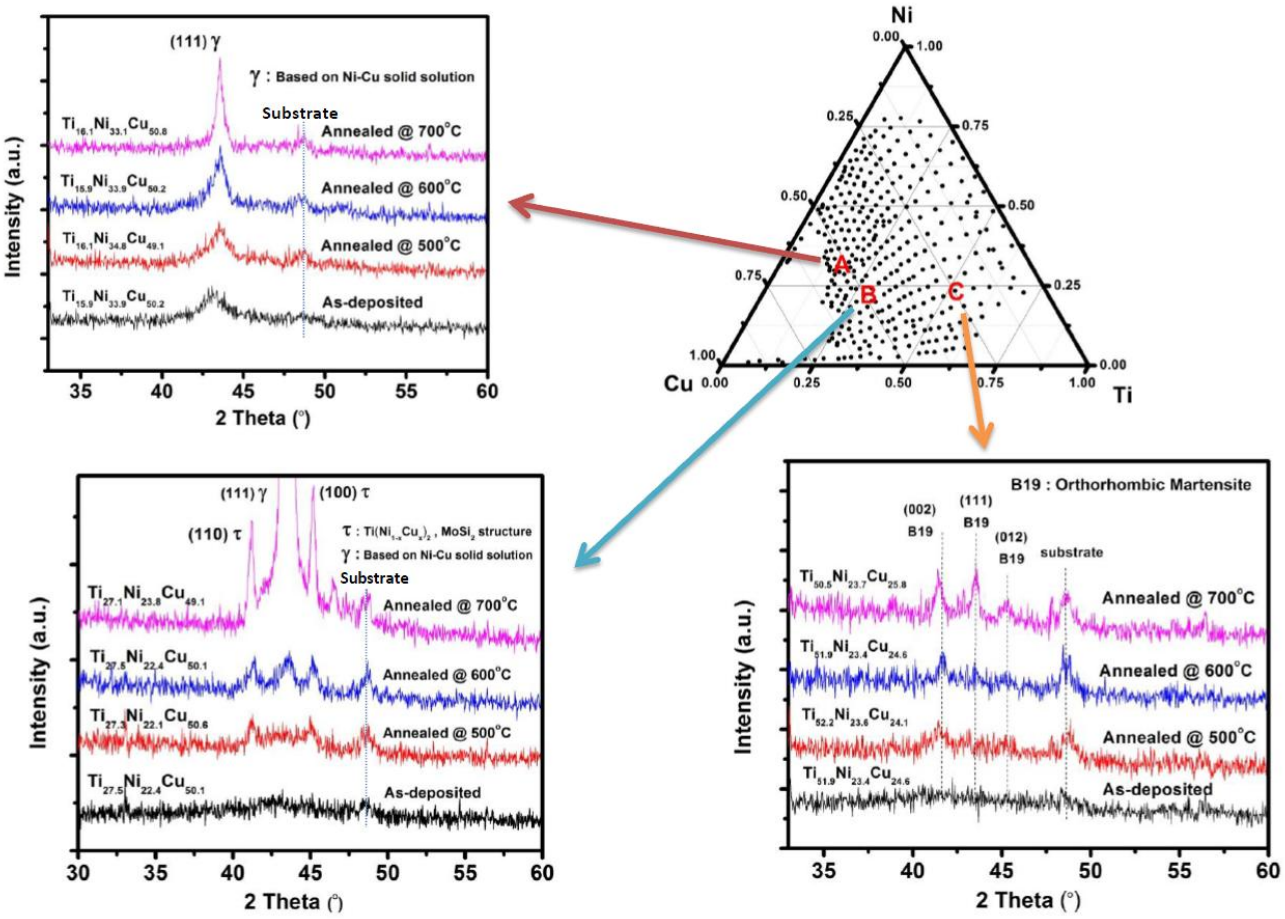


Figure 36: Phase identification and peak indexing of selected compositions within a Ti-Ni-Cu combinatorial library as a function of post-deposition UHV annealing temperature of separate but identical libraries. All heat treatment times were of 1 hour duration.

Although specialized computer software for the analysis of large XRD datasets exists[14], considerable manual data manipulation such as background subtraction and peak selection/designation must still be done for each spectrum, particularly in the case of searching for amorphous regions.

Therefore, resistivity measurements are being investigated as a very high-throughput, fine measurement grid spacing method for screening, based on the phenomenon that a change in resistivity generally accompanies a change in phase. Thus the amorphous-to-crystalline transition could be detected by comparison of before and after heat treatment measurement maps (

[14] I. Takeuchi, C. J. Long, O. O. Famodu, M. Murakami, J. Hattrick-Simpers, G. W. Rubloff, M. Stukowski, and K. Rajan, *Rev. Sci. Instrum.*, **2005**, *76*, 62223.

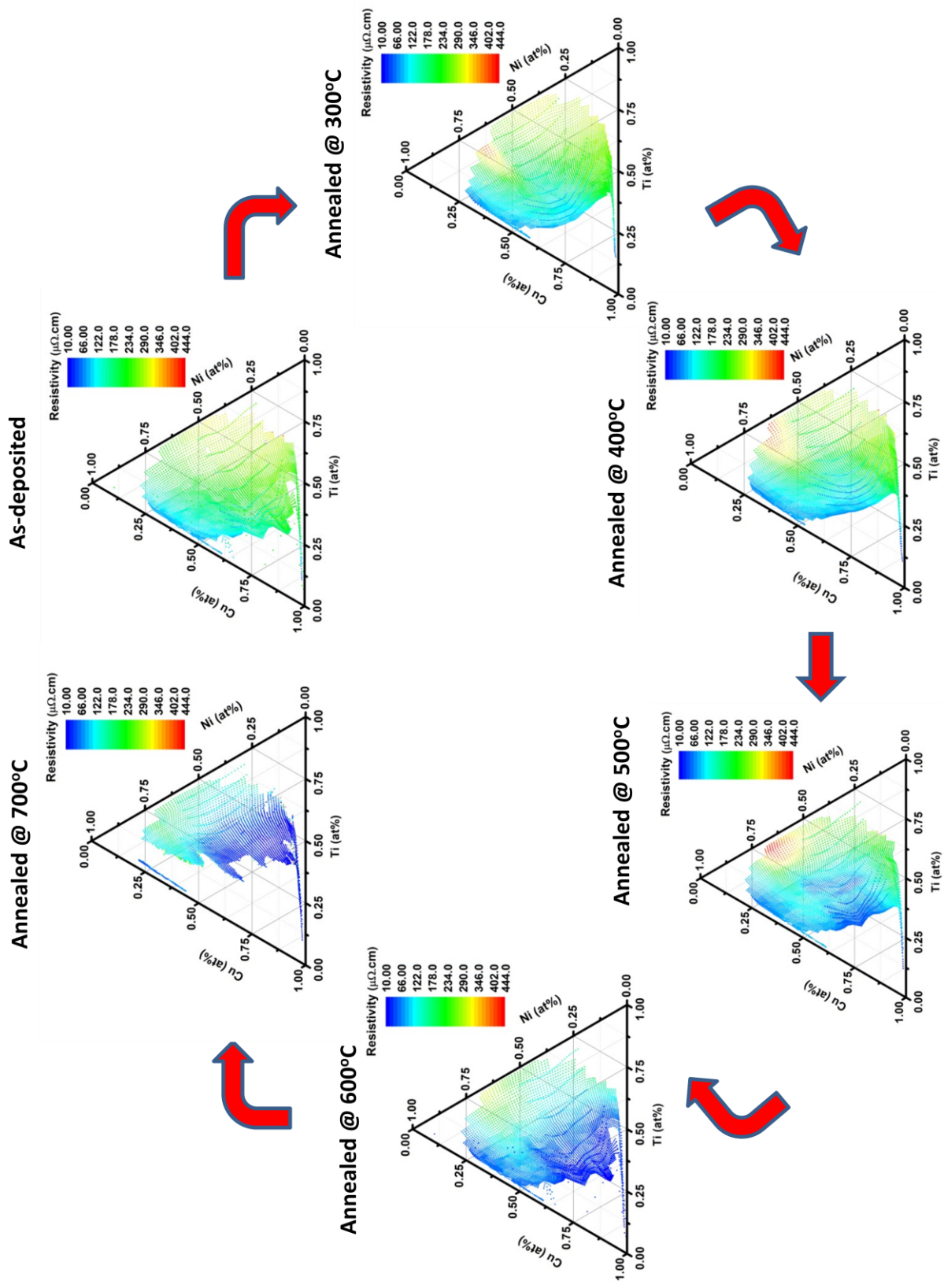


Figure 37).

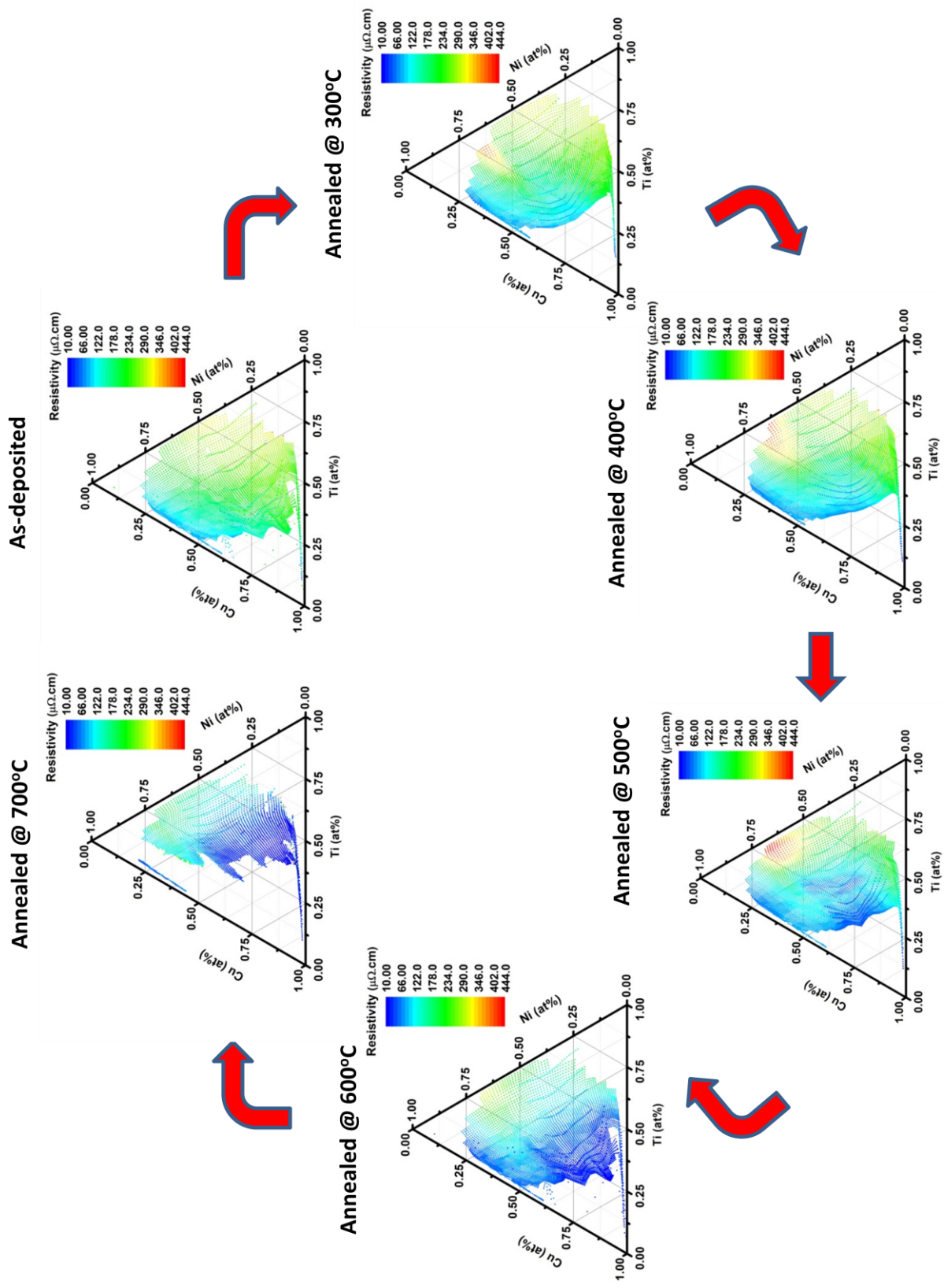


Figure 37: High-throughput 4-point probe resistivity maps of Ti-Ni-Cu combinatorial libraries. The libraries were identically deposited in batches of 5 and then UHV annealed for 1 hour at the temperatures indicated, then measured in air at room temperature.

As discussed in Section 4.8, hardware is being developed to enable *in situ* measurements of resistivity by the 4-point probe technique, during annealing (Figure 29). Substantial questions about the reliability and stability of multiple sets of 4-point probes at high (> 600°C) to very high (> 900°C) temperatures are still to be resolved. Precise movement with repeatable and uniform probe force is a problem at such temperatures, so the goal at this time is to scale up from 12 probes (i.e. 3 sets of 4-point probes, Figure 28) to as many as 100 sets, however without scanning capability.

Considerable work remains to establish and validate conditions and criteria that correlate resistivity data with XRD and TEM analyses, but the value for high-throughput and *in-situ* screening is compelling.

The data measured from the Ti-Ni-Cu combinatorial libraries are being prepared for presentation and publication at the Materials Science Engineering (MSE) conference sponsored by the German Research Foundation (DFG), to be held in Darmstadt, Germany, 25-27 September 2012 (http://www.dgm.de/dgm/mse-congress/).

The Amorphous Range in Sputtered Ti-Ni-Cu Combinatorial Thin-Film Libraries

Y. Motemani, A. Savan, S. Thienhaus, Y. Al-Zain, A. Ludwig

> Amorphous materials are the subject of intense investigation due to their desirable mechanical properties, including high hardness and yield strength, high corrosion resistance, and their formability. Recently, there is also interest in using these materials in MEMS applications. This study presents a search for Ti-Ni-Cu thin film amorphous alloys using high-throughput screening methods for finding the amorphous-crystalline transition in a combinatorial library. A large portion of Ti-Ni-Cu ternary diagram was synthesized at room temperature by deposition of repeating wedges of a few nanometers thickness from elemental targets. Five identical libraries were deposited simultaneously enabling direct comparison after annealing treatments. In the as-deposited state, large areas of the grown libraries were amorphous. The composition distribution over the libraries was analyzed by automated energy dispersive X-ray analysis (EDX). The crystallinity of the samples was investigated by automated X-ray diffraction (XRD). Heat treatments at 300°, 400°, 500°, 600° and 700°C were employed to evaluate the thermal stability of amorphous domains within the thin-film libraries. *Ex-situ* high-throughput resistivity measurements were used to investigate if the amorphous-crystalline transition could be detected with this technique. Finally, candidate amorphous compositions with the highest thermal stability were identified for future studies with bulk materials.

5.2. Nb-Cr-Si

A set of 5 identical combinatorial libraries of Nb-Cr-Si were deposited using the aperture-shaped deposition technique (Section 3.3). One of these libraries was set aside for the as-deposited reference, one was deposited on an Al_2O_3 substrate for EDX analysis, while 3 others were separately annealed in ultra high vacuum (UHV) at 500°, 600° and 700°C respectively, each for 1 hour with a 50°C/minute heating rate (Figure 38).

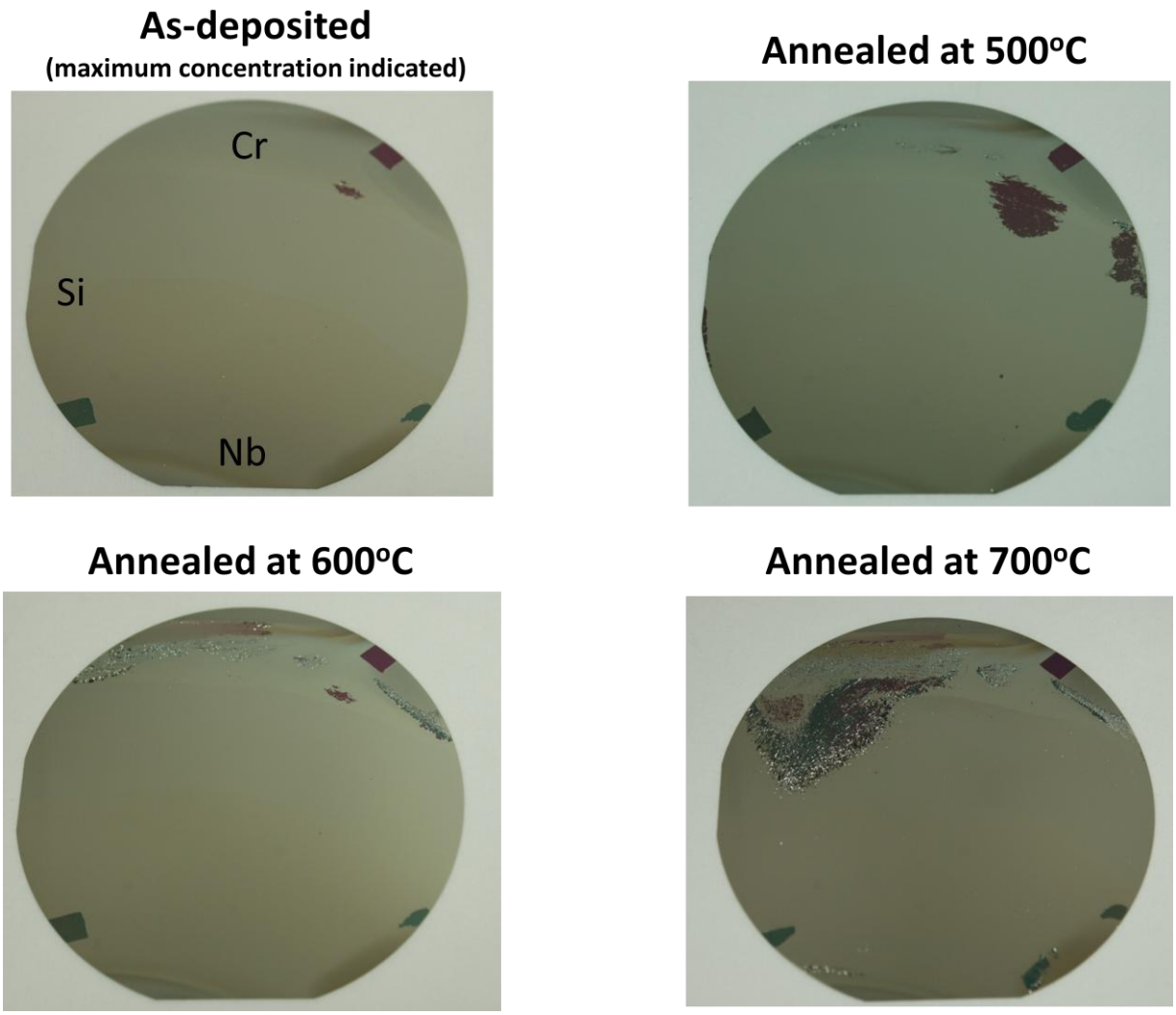


Figure 38: Photographs of identically deposited Nb-Cr-Si combinatorial libraries as deposited, and heat treatments at the indicated temperatures in UHV for 1 hour.

The thickness distributions of each individual element were characterized with respect to their respective apertures (Figure 39). Since the geometry of the PVD system does not permit the full ternary composition space to be covered with a single deposition, maps of each element allow the general location of the compositions produced to be re-located within the ternary diagram. Individual point compositions were mapped with automated EDX and are plotted in a ternary diagram in Figure 40(a). Automated XRD was then used to make a generalized grouping of the amorphous and crystalline/partially crystalline regions in the library (Figure 40b).

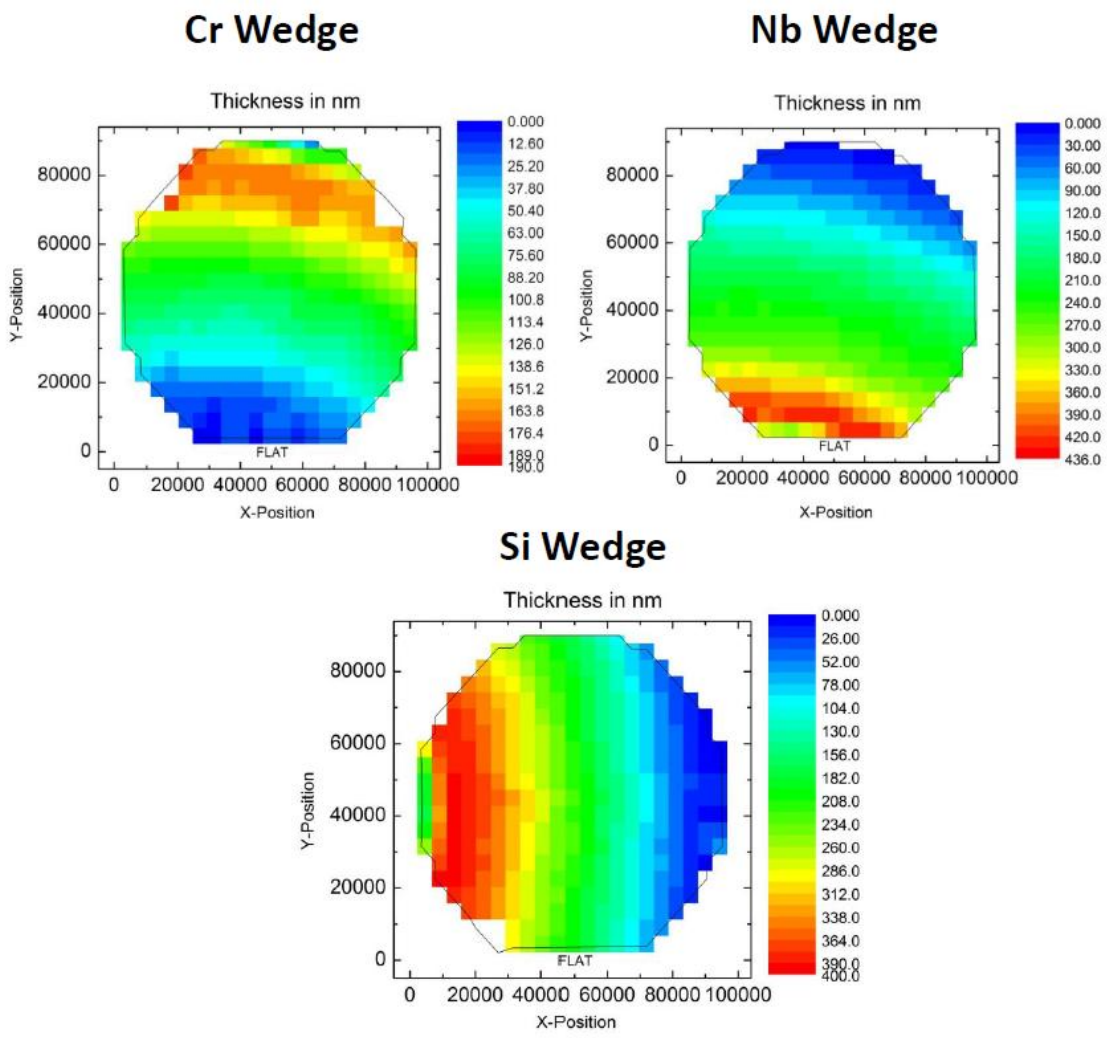
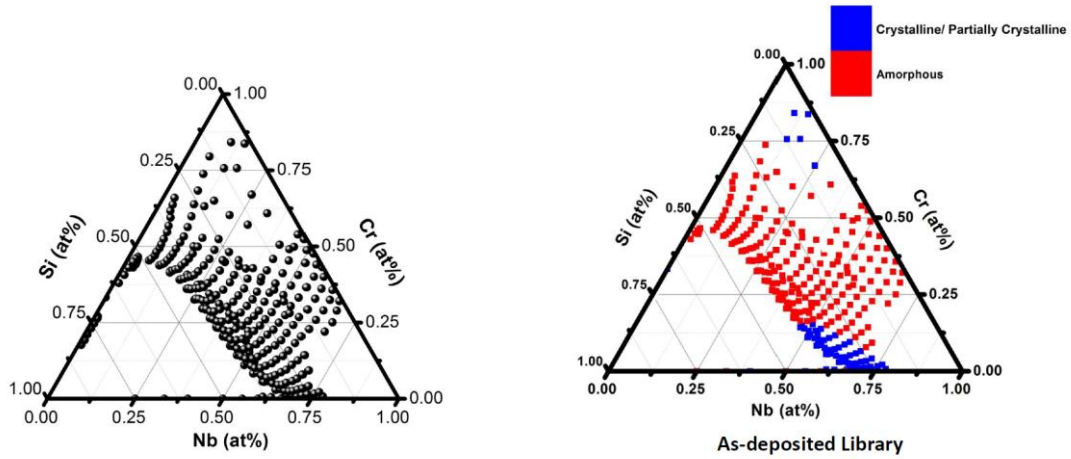


Figure 39: High-throughput mapping by stylus profilometry of individual Nb, Cr and Si depositions, showing the direction and gradient for each element.



(a) (b)

Figure 40: (a) Composition range of the Nb-Cr-Si combinatorial libraries, from EDX data. (b) Library color-coded as amorphous or crystalline/partially crystalline, based on XRD mapping and analysis.

Selected areas identified as being crystalline or polycrystalline in the as-deposited library were then chosen, and compared with the same points in the annealed libraries (Figure 41).

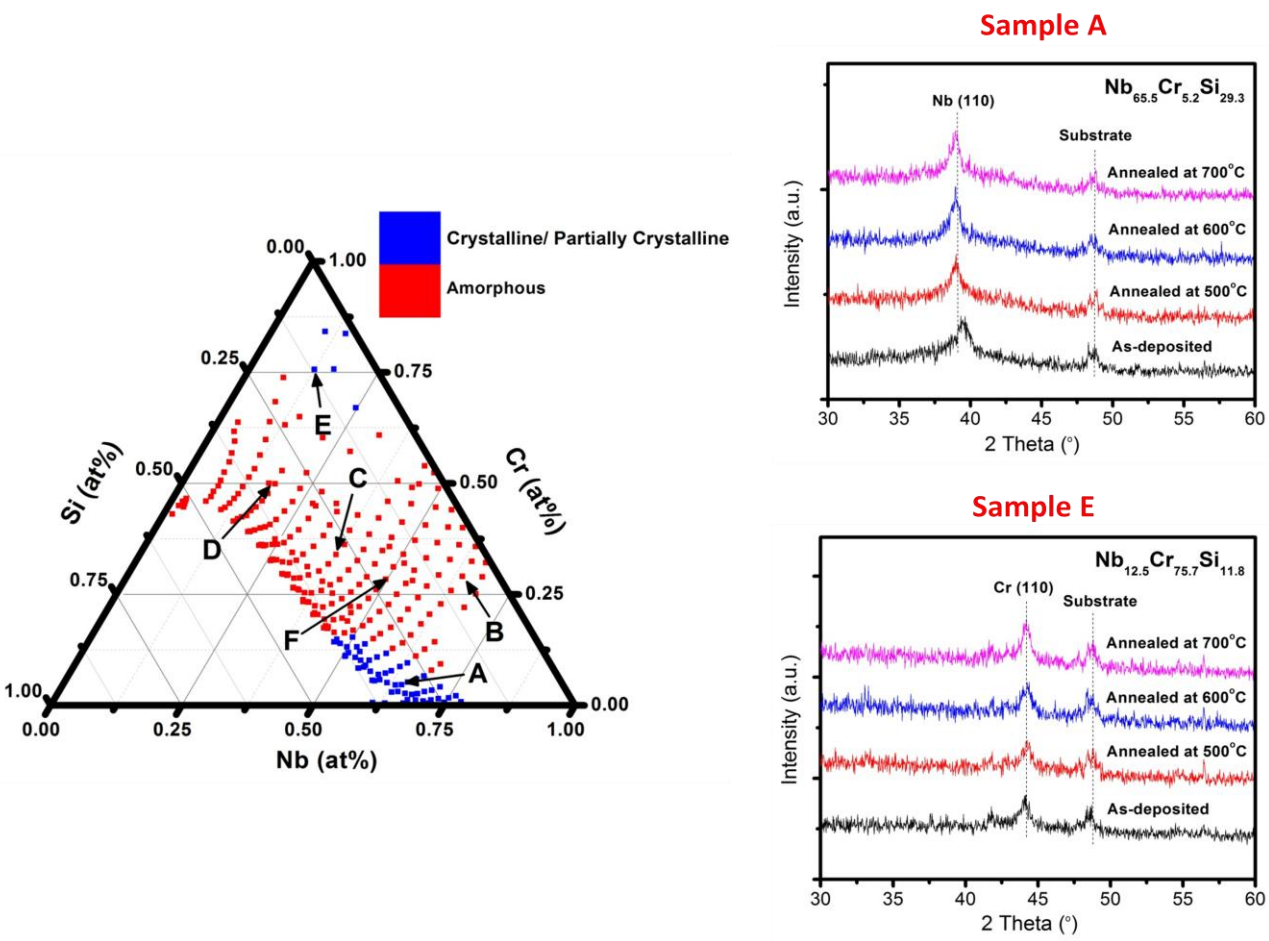


Figure 41: Comparison of XRD spectra from 2 representative areas that were identified as crystalline/polycrystalline as deposited ("A" and "E"), after annealing at the indicated temperatures.

Similarly, areas identified as being amorphous based on their XRD spectra in the as-deposited state were compared after annealing at 500°, 600° and 700°C for 1 hour in UHV conditions. Figure 42 indicates little if any change, suggesting that the "amorphous" structure is stable up to 700°C for this heat treatment.

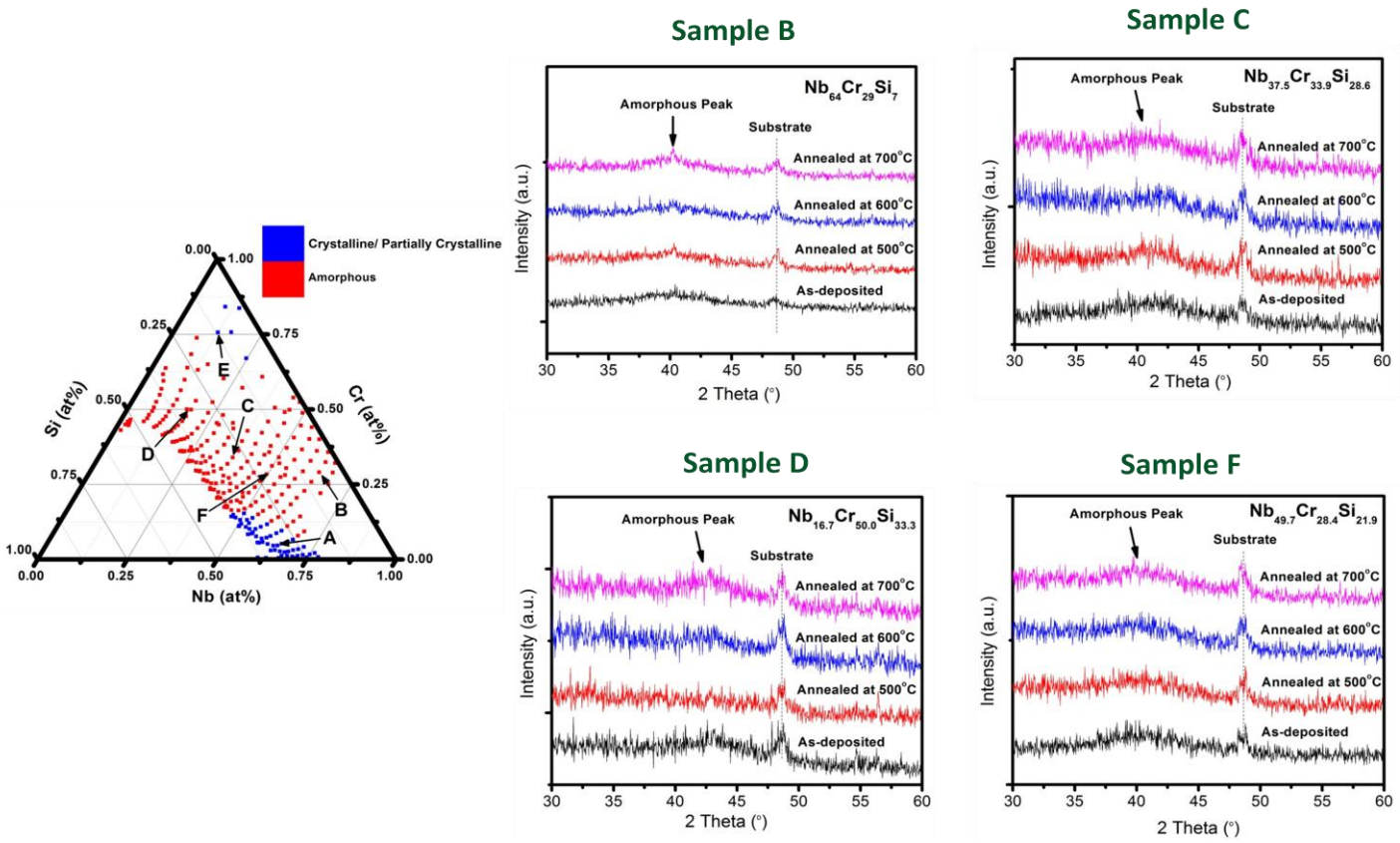


Figure 42: Comparison of XRD spectra from 4 representative areas that were identified as amorphous as deposited ("B", "C", "D" and "F"), after annealing at the indicated temperatures.

Figure 43 shows a test of high-temperature corrosion resistance, where a combinatorial library of Nb-Cr-Si was exposed to air for 1 hour at increasing steps in temperature, with optical images recorded after each step (with the library cooled back down to ambient temperature).

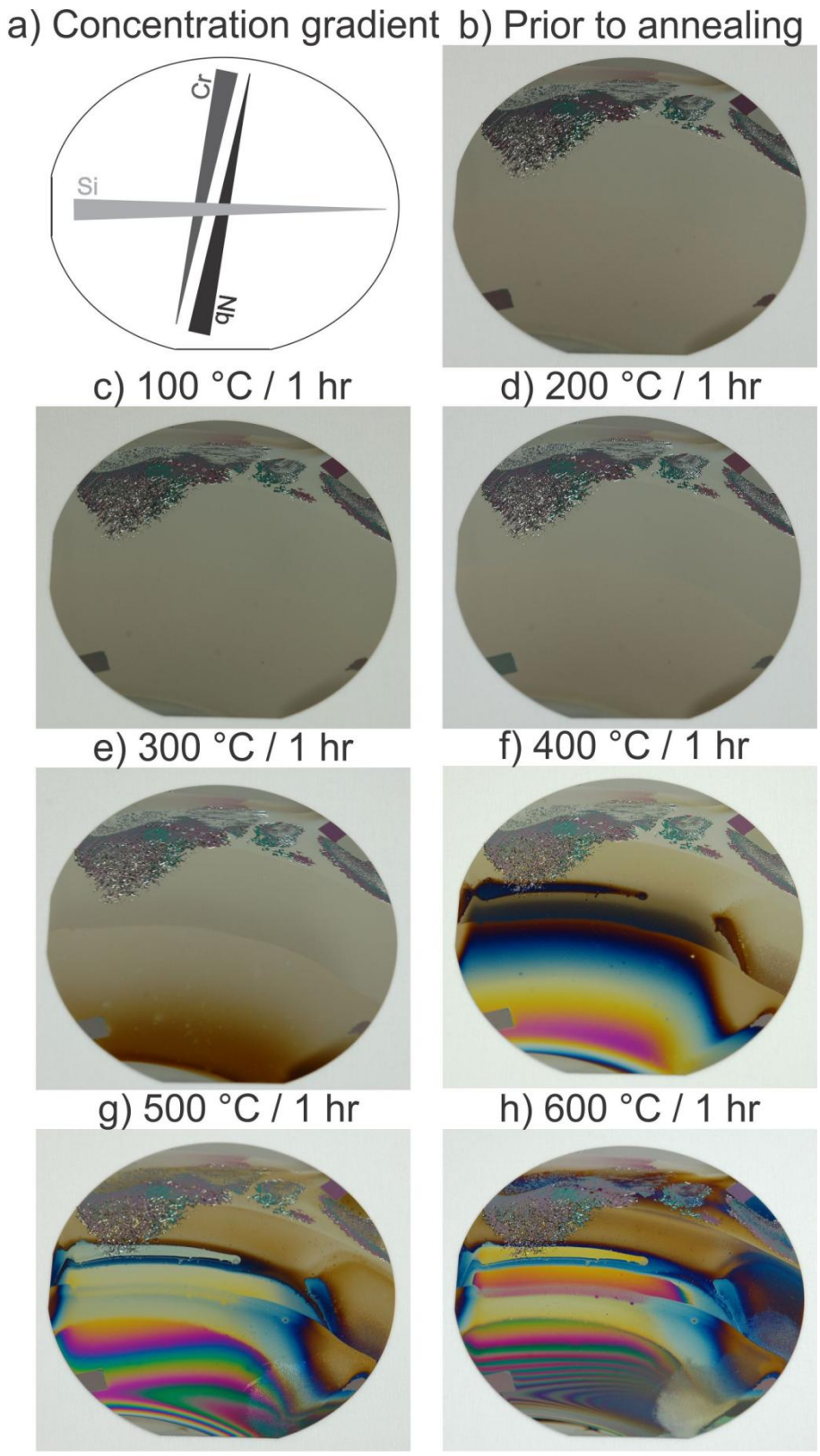


Figure 43: (a) Schematic diagram indicating the directions of the Nb, Cr and Si composition gradients. (b) Nb-Cr-Si combinatorial library, as deposited at ambient temperature. (c - h) Images of the same library after additional heat treatment in air as indicated.

It is planned that a publication will be prepared related to the Nb-Cr-Si combinatorial library, when measurements and data analysis is completed.

6.0. Evaluation of High-Throughput Screening Techniques

6.1. Resistivity vs. Temperature Mapping

Test versions of a high-temperature 4-point probe measurement head were built and installed in a vacuum chamber that was equipped with a small heater capable of reaching 600°C. Different probe tips, ceramic materials for holding them, high-temperature cements and insulation, and connectors were tested.

The hardware seems to be feasible at least to 600°C. It is not clear if a mechanism with more 4-point probes – up to 100 probe sets – can be made that makes repeated, precise contact with sufficient and uniform force at all 400 points in vacuum and at high temperature. However there are no obvious impediments to starting a scale-up towards that goal, which is currently underway. It is also not known if the probes or the substrate could be moved relative to one another in those conditions, or if the measurement should be restricted to a simultaneous measurement at multiple points along a single line.

In terms of measurement data, some of the test measurements show significant noise while others do not. It is considered that this may come from a surface oxide, and how the probes contact and penetrate this oxide (or not), and if they scratch deeper or even through the film. Further work is underway with curved and straight probe pins, different pin materials and pin movement/loading mechanisms to clarify and address these issues.

The long-term stability and reproducibility of the measurement hardware and data have not been proven. However neither are there any insurmountable obstacles discovered so far that prevent achieving accurate and reliable measurements.

In terms of data, resistivity versus temperature can provide indication of crystallization, at least in some materials systems. The actual microstructure or other cause(s) of resistivity changes must be clarified by other measurement techniques to make an unambiguous determination, however once that is done, resistivity versus temperature can provide an invaluable *in-situ* high throughput screening method.

6.2. X-ray Diffraction Mapping

While XRD mapping is automated, data collection for a 4-inch wafer takes approximately 15 hours, compared to about 4 hours for automated thickness mapping by stylus profilometry or 5 to 8 hours for automated EDX mapping. However while data from the latter 2 measurements is quickly formatted and graphed, the data analysis for XRD evaluation is extremely time-consuming and requires the attention of someone with considerable expertise with the technique, the materials being analyzed, the hardware used and several different software packages.

XRD is nonetheless a critically important tool in these investigations, because it is still the most feasible method to detect crystallinity and determine the phases that may be present. Therefore

methods are being developed to screen large XRD data sets in order to identify and extract a limited number of points for detailed analysis.

This possible methodology for rapid screening of materials libraries is being further investigated and refined with the aim to establish guidelines and boundaries for applicability. However it is a step in the direction towards developing high-throughput screening methods for large combinatorial materials libraries.

6.3. Optical Reflectivity Change Detection

Optical observations or measurements are inherently high throughput as well as being non-destructive, non-contact and (generally) possible *in situ*. These advantages make optical response a very attractive technique to use with combinatorial libraries. However this is a method that only applies to some materials systems and to some composition ranges within them. It also requires careful analysis and interpretation of the results, in that the optical response may come from several physical or chemical mechanisms, or combinations of them.

The tests to date in this project tend to confirm both the excellent utility of optical monitoring (reflectivity changing region in a TiNiCu library, onset and progression of oxidation in a NbCrSi library) and the need to use it in coordination with other measurements and analyses in order to interpret and understand the results. After an understanding of the mechanisms leading to the changes detected by optical monitoring is developed, this method has great promise to be a very fast technique for identifying regions of interest in combinatorial libraries of materials systems exposed to harsh environment testing.

6.4. Cantilever Bending for in-situ Stress Measurement

Cantilever bending enables the in situ detection of stress changes during high temperature annealing and corrosion (oxidation). The measurement of the cantilevers needs a window, which increases the complexity and can influence the maximum temperature and temperature uniformity performance of a high-temperature test stand. Another issue is that cantilever bending is in general the cumulative result of what may be several mechanisms. Similar to optical monitoring, additional measurements and analysis is required to ascribe particular features of the cantilever response to specific behavior, such as an amorphous to crystalline transition. However in materials systems where such a link is established, it then becomes a considerably faster and simpler screening method for materials libraries than, for instance, x-ray diffraction or TEM.

6.5. Digital Holographic Measurement

Digital holography is of interest for further development because it can acquire each image within seconds, and the effects of long-scale wafer curvature can be removed. It therefore has promise to be a faster technique than point-by-point scanning with profilometry, as well as not being sensitive to potential single-point defects such as particle, pinholes or local substrate curvature that complicate or prevent stylus measurements.

6.6. High Temperature Corrosion Detection and Measurement

Realization of an effective high temperature corrosion test stand will require a purpose-built ultra-high vacuum chamber equipped with a loadlock. Thus high-temperature annealing can be done without unintentional oxidation occurring from outgassing of the chamber walls and fixtures, and the sample itself. Mass flow controlled gas inlets can then be used to make controlled and repeatable corrosion studies.

7.0. Status and Outlook

Thin film combinatorial libraries of two different ternary materials systems have been deposited. For both Ti-Ni-Cu and Cr-Si-Nb systems, multiple libraries were produced, so that different analyses, different annealing treatments, and corrosion studies could be performed on identical materials, while also having an as-deposited reference library. The preparation of two publications is underway, as data analysis and possibly further measurements are being completed.

A wide range of high-throughput measurement and characterization techniques have been developed and tested with the combinatorial libraries, in order to evaluate their feasibility and applicability for *in-situ* and *ex-situ* high-temperature annealing, crystallization and corrosion studies.

Based on the experience gained from these studies, a suitable test stand for high-temperature annealing and corrosion measurements and screening of combinatorial materials libraries was designed. While full fabrication and realization was beyond the budget and time of this project, critical elements of such a test stand and measurements have been built and tested, and are continuing to be refined.

It is seen that a wide range of measurement and characterization techniques must be implemented to a loadlocked, ultra-high vacuum testing chamber that additionally has gas and pressure control capability, in order to have a general purpose facility for the high-throughput screening of complex combinatorial thin film libraries for the identification and development of novel high-performance materials for critical applications.